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New Principle Proposed for

Wool Dyeing*

THERE is no doubt that the woolen industry has been greatly impressed by the discovery,† and the next step—commercial application—is eagerly awaited. We understand that the next two months will see the introduction of large-scale working. No profound change in the construction of machinery is anticipated. The engineering firms are studying the matter very carefully and it is expected that in most cases modifications to existing plants will meet the demands of the method.

Patents have been applied for in connection with the process.

The fundamental principle of the new technique is that a controlled turbulence of the dye-liquor during dyeing of wool is conducive of rapid dyeing and good penetration. It is therefore proposed to create this controlled turbulence in the liquor in applying dyestuffs, especially with certain troublesome dyes or materials, so that the material is bombarded by dye-liquor and air. This action results in a reciprocating pumping of liquor through the wool and a vibration of the individual fiber scales which causes them to take in the dye. The process, it is claimed, enables wool to be dyed at from 60 to 80° C., at atmospheric pressure, in a shorter time and with better results both as regards the dyeing itself and the quality of the dyed wool than has hitherto been possible. Alternatively, reduced pressure can be employed and even lower temperatures are then made permissible. In both cases, however, the vital point is the turbulence of the liquor.

The process owes its origin first to the fact that H. Jackson, Chief Colorist to the B.D.C., and D. Carter, Assistant Chief Colorist, considered that it was desirable to know whether 100° C. really represented the best temperature for dyeing wool. It was felt that it was rather an extraordinary coincidence that the boiling point of water should be the ideal temperature for dyeing wool. It was naturally anticipated that if wool could be dyed at lower temperatures than 100° C., it would be of superior quality, since normal boiling admittedly deteriorates wool, particularly from the point of view of strength.

Mr. Carter suggested that dyeing in a partial vacuum should be employed in order to achieve a boiling of the dye-liquor at temperatures below 100° C. Experimental work demonstrated that a superior rate of dyeing and penetration of felt by color was achieved by dyeing with some acid and chrome dyestuffs at 80° C. at a diminished pressure of 280 millimeters. Dyeing experiments at 60° C., and 40° C., in dye-liquors boiling at low pressures were also successful with some acid dyestuffs.

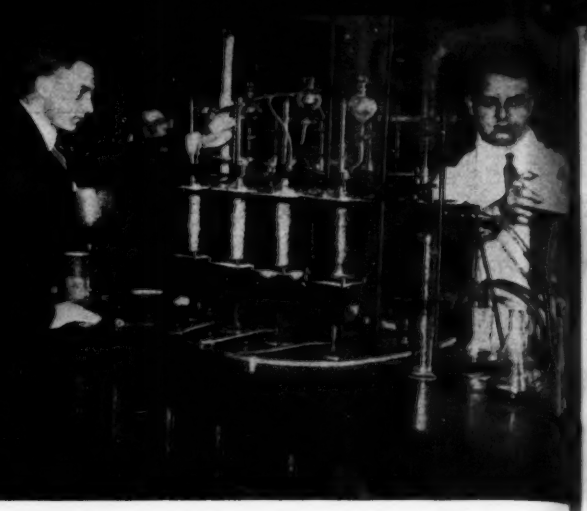
H. A. Thomas, of the Dyehouse Laboratories, while working on this subject, then discovered that by drawing air through the dye-liquor during dyeing, or by bubbling compressed air into the dyebath so that a vigorous turbulence of the liquor was achieved, improved dyeing results were obtained at atmospheric pressure, at tempera-

†There has been demonstrated at Bradford, England, quite recently, a new system of dyeing woolen material. It was first described before the Society of Dyers and Colourists in Bradford on Thursday, February 21st, and was again demonstrated February 25th before a large representation from the woolen industry of England. The process was worked out in the laboratories of the Imperial Chemical Industries, Ltd., at Blackley, England.

Dyeing may be carried on at a temperature of 140° to 176° F. and secure better penetration in a shorter time than may be obtained at a boiling temperature under the usual conditions of dyeing. The method consists of a controlled turbulence of the dye liquor which gives an agitation in the dye liquor which might be compared to the movement of a dye liquor being violently boiled at 212° F. The process is described by the originators as a bombardment of the textile material by the dye liquor and air. The process is claimed to have many advantages over the older method and has created no little interest among dyers in England and gives promise of a decidedly new development in the technique of dyeing wool.

*This article is abstracted for the most part from *The Dyer*. The illustrations are published through the courtesy of that journal.

This photograph was taken during a demonstration of the new wool dyeing process in the chemistry lecture theater of the Bradford Technical College. H. A. Thomas is second from the right behind the bench, in front to the left of his assistant are H. Jackson and D. Carter.



H. A. Thomas and his assistant demonstrating the new wool dyeing process at Bradford.

tures below the boil. Thick wool fabrics, including felt, were satisfactorily dyed in the laboratory at temperatures of 80° C., and also with some acid dyestuffs at as low a temperature as 40° C. A comprehensive investigation showed that the improved rate of dyeing and penetration of fabrics was due to the turbulence in the dye-liquor, which caused a bombardment of the wool by dye. This produced the effect of pumping the dye-liquor into the wool fabric, and also a vibration of the individual wool fibers, which can be said to "breathe in" the dye. This latter effect was observed with an individual wool fiber under the microscope.

A. G. Cuthbert-Smith, also of the Dyehouse Department, demonstrated that this vibration effect was beneficial in dyeing, by connecting the wool fabric during dyeing to an electrical vibrating machine.

It is expected that the discovery of the importance of a turbulent effect in dyeing, will lead to the wide use of new mechanical devices for obtaining a controlled bombardment of the wool with dye-liquor. The simplest application of the principle appears to be by a controlled air-bubbling, and L. P. Rendell has shown how the method could be advantageously applied in winch machines, chiefly for the dyeing of wool piece, especially thick felted fabrics.

At the demonstration on February 25th, most of those associated with the discovery were present and a brief introduction to an address by Dr. Thomas, who conducted the experiments, was given by H. Jackson, Chief Colorist to the B.D.C. He said that the process was the result of an organized attack which they were making on problems of dyeing in all industries. It was more or less the first egg out of the basket and they were hoping to hatch quite a number of others later on.

This new technique in wool dyeing had he thought, demonstrated very forcibly that one could not take long-established practices as being the last word. They had approached wool dyeing from a new angle with, they considered, very promising and interesting results. They hoped as a consequence of their investigations to throw open for use quite a range of dyes which were not hitherto available to the hat dyer and to wool dyers generally.

They believed that, quite apart from the manufacture of dyes, it was incumbent upon them to provide new means of using already-existing tools. They thought that this new technique would make the textile trade generally look at things from a rather different angle than it had in the past, and they looked forward to big developments which would enable textile people to hold their own against competitors, because they believed that one very fundamental fact was that the success of the textile trade was their success.

Dr. H. A. Thomas then proceeded to explain and demonstrate the new process. He pointed out that they were constantly seeking new and improved methods of dyeing. In such considerations, the effect of the dyeing process on the quality of the textile fiber was of real importance, and this was especially the case with wool, where the nature of the fiber must be preserved in order that its value may not be lowered appreciably.

It was well known that boiling water (at atmospheric pressure, 100° C.) had a detrimental effect on wool. The usual method was however, to bring the dye liquor to the boil. It would be a remarkable coincidence if boiling temperature were the most suitable.

It was obvious that a temperature below 100° C. would be a great benefit and they therefore began extensive investigations involving 2,000 dyeing experiments and trials with some 52 representative dyestuffs of all classes employed in wool dyeing. They employed temperatures from 40 to 100° C., and found that temperatures from 60 to 80° C. were quite satisfactory for dyeing wool with most dyes, *provided that ebullition or turbulence of the liquor was induced.*

There was in ordinary practice some turbulence in the boiling dyebath, but it was never recognized until the results of their work came to light that this ebullition of the liquor was really an important factor during the process of dyeing at the boil. They found, of course, that by working at lower pressures they could still produce this vigorous ebullition. As they knew, under partial vacuum,

one could boil water at temperatures much below 100° C. They had in their experiments used liquor boiling at 40° C., at a pressure of 55 mm. There was an important point to be noted here. Under reduced pressure, say, at the top of a mountain, one could not cook an egg in boiling water, yet it was found that wool could be dyed at these lower temperatures and pressures quite satisfactorily, provided the turbulence was present.

They then found, continued Dr. Thomas, that by inducing this same turbulence at atmospheric pressures, by bubbling air vigorously into the liquor, they could obtain the same satisfactory results at temperatures well below 100° C. The important fundamental principle was that turbulence in the dye liquor was an essential factor of satisfactory wool dyeing and provided this was present it was not necessary to raise the temperature to 100° C.

This discovery, asserted Dr. Thomas, had far-reaching consequences. It was possible with a large number of dyes to obtain much more satisfactory dyeing results, as well as improving the condition of the wool, at temperatures from 60° C. to 80° C., than had hitherto been obtained by the customary methods. The most important effect of the technique had been aptly described as a bombing action of the wool and a vibration or throbbing on the part of the fibers was set up. They came to this conclusion by investigating a single wool fiber under the microscope. The behavior of the scales was watched; they appeared to vibrate and thus enabled the dye to enter into the cortex.

Besides these effects which turbulence brought about, there was undoubtedly an improvement in the physical condition of the liquor and the properties of the dyed material depended largely on the physical condition of the liquor. The dye must be in a fine condition in the dye-liquor. Dr. Thomas explained that the condition of the dye could be ascertained by tests with filter paper. The higher the paper was stained the finer the particles; if the paper was stained only a short way, with water continuing to soak up the paper, the coarser the particles. Dye-liquor in which turbulence had been promoted colored filter paper to a much greater extent than liquor in which there was no turbulence, showing that the dye was in much better physical condition, which led to much better dyeing properties and fastness properties.

There was a possibility, Dr. Thomas went on, that with some wool materials there was a liquid film over the scales which prevented the dye getting in. This was undoubtedly broken down by the bombardment by the bubbles or the vigorous turbulence.

The actual results obtained, he pointed out, demonstrated the advantages over customary methods. First of all, one obtained much more rapid dyeing. Thick materials, such as felt, were very difficult to penetrate by the normal methods, even with some of the best penetrating dyes and it was necessary to boil for long periods in order to get the color right into the felt. If dyeing were only carried out for a short period the inside of the felt was quite white, the color being merely on the surface.

With the new technique it was possible to get complete penetration in 10 to 15 minutes, even with colors which were not normally satisfactory for dyeing thick wool felt, but were used for dyeing wool where penetration was not really important. Dr. Thomas said that in the practical demonstration—which was carried out during the latter part of his address—they would use two dyes which did not usually penetrate felt satisfactorily, and it would be shown that by applying turbulence they could obtain satisfactory penetration at 80° C., atmospheric pressure, and obtain wool in a much more satisfactory condition.

Dealing with further advantages of the process, Dr. Thomas observed that they got a more complete exhaustion of color from the dyebath.

With thick materials it had been necessary to use selected dyes. By applying this technique one did not have to worry so much about selection. It widened the whole range of colors which could be applied and was therefore a very important step forward. It meant, for instance, that the felt dyer had at his disposal a method which would enable him to use a much more extensive series of dyes.

It was important both as regards penetration and at the same time, exhaustion of the liquor.

It was really quite unusual, he observed, because it was known that if material was dyed very rapidly all the color rushed on to the surface of the fiber and, in the case of thick materials, the inside was not dyed at all. Previously the way to get good penetration was to dye slowly. In the new technique, however, they speeded up the rate of dyeing and at the same time obtained an improvement in penetration.

Dr. Thomas passed round for examination comparative pieces of felt (cut so as to expose the center), showing the effects obtained by dyeing by the new and by the older methods. The superior penetration brought about by turbulence of the liquor was very striking. Among the colors which had been applied to these samples were: Solochrome Yellow 2GS, Coomassie Yellow RS, Coomassie Brilliant Blue FFS, Chlorazol Yellow GS, Lissamine Green VS, Solochrome Orange MS, Naphthalene Black 12BS, Coomassie Milling Scarlet 5BS. The dyeings had been carried out at 80° C., atmospheric pressure, with ebullition; at 80° C. under reduced pressure; and by the usual methods.

Dr. Thomas went on to comment on the process being carried out on the bench. Some of the felt was being dyed at the boil in the ordinary way, while compressed air was being bubbled into some of the flasks and in others the process was proceeding under vacuum. The dyes being used were Coomassie Milling Scarlet 5BS and Naphthalene Black 12BS.

While the dyeings were under way, Dr. Thomas called attention to still further advantages of the new technique relating to individual dyes. With many dyes, he said,

they obtained brighter shades. There were one or two dyestuffs which were not really satisfactory for applying at too high a temperature and by applying the new method they could work at lower temperatures. One dye of great interest was Coomassie Navy Blue 2RNS, which gave a brighter blue.

Dr. Thomas then referred to the results of some tensile strength tests on worsted yarn. They found that there were very big differences according to the method of dyeing. First, they tested the strength of undyed yarn and yarn dyed by the normal boiling, and found that there was a big decrease in strength in the dyed yarn. Then they tested yarn dyed at atmospheric pressure at 80° C., with air bombardment, and yarn dyed under reduced pressure. That dyed with ebullition under reduced pressure was very little altered in strength, while that dyed with air bubbling through at 80° C., also had a very satisfactory tensile strength.

In connection with the turbulence, Dr. Thomas pointed out that it must be controlled in some way. Swirling of the liquor and the material must be prevented. In practice they could obtain this controlling of the ebullition. It consisted of a bombardment with dye-liquor containing air.

Turning to vat dyes, Dr. Thomas said that naturally air could not be bubbled through the liquor, but they could get over that difficulty by employing an inert gas, such as carbon dioxide, or the ebullition technique could be worked under partial vacuum.

He emphasized that while the experiments were being made with felt, the process was applicable to all other forms of woolen material.

George Hopkinson, Honorary Secretary of the Society of Dyers and Colorists, in proposing a vote of thanks to Imperial Chemical Industries and Dr. Thomas, declared that as a wool dyer of 25 years' standing he could tell them that this was one of the most revolutionary discoveries ever made in wool dyeing. The lecture on the previous Thursday had, he said, created a great impression on the members of the industry present.

● MOVE SALES OFFICES

Effective May 1, the New York Sales Office of Republic Steel Corporation will be removed to the Chrysler Building, according to an announcement by N. J. Clarke, Vice President in Charge of Sales for Republic.

W. H. Oliver continues in charge of the office as District Sales Manager. Republic's Export Department, under the direction of D. H. Bellamore, General Export Manager, will also occupy a portion of Republic's new suite in the Chrysler Building.

● GENERAL RELEASES

The General Dyestuff Corp. announces release of bulletins on the following products. Copies are available upon request.

Anthra Cyanine Violet 4 *B*—a new level dyeing acid color, said to produce bright shades of violet of better fastness to light than the ordinary acid violets. It is further said to be of good fastness to carbonizing, decatizing, stoving, rubbing and hot pressing, and of fairly good fastness to perspiration, washing and fulling. It is said to exhaust well from a neutral bath, and is recommended by the distributors for brightening the wool in union dyeing. It is further stated that this dyestuff is suitable for dyeing pure silk and silk-wool mixed fabrics, and, as the shade is only slightly dulled by chrome, it may be used for brightening the wool in dyeing shoddy, etc.

Diazo Brilliant Blue B B L A—a developed color of a very bright greenish blue shade, said to be well suited for discharge work and for dyeing mixed fabrics of cotton and rayon in the same tone. It is stated that this dye leaves acetate unstained.

Benzo Fast Orange W S A—a direct dyestuff manufactured by the General Aniline Works, which is said to produce on cotton and rayon very bright shades of very good fastness to acid and good fastness to light, leaving acetate clean.

Celliton Discharge Scarlet R L—said to be a very bright shade on acetate which discharges easily, and is also recommended by the distributors for application prints.

● BUSINESS PUBLICATIONS

Liquid Chlorine—a booklet published by the Solvay Sales Corp., which includes among other items a history of liquid chlorine, chlorine constants, properties of chlorine, equipment for handling chlorine, and chief uses of chlorine. The preparation of soda bleach liquors and lime bleach liquors is discussed in detail. There are numerous charts and graphs giving further information.

World's Largest Plate Mill and Its Products—a publication of the Lukens Steel Co., which is a pictorial summary of this company and its divisions — By-Products Steel Corp. and Lukenweld, Inc.

Enduro 18-8—a booklet of the Republic Steel Corp., which contains data on various stainless steels, such as Enduro 18-8, Enduro 18-8-S, Enduro, 18-8-STi, Enduro 18-8-SMO, Enduro 18-8-B and Enduro 18-8-FM. A table is given showing the resistance of several types of stainless steel to various chemicals. Booklet No. 125-A.

● COLGATE CONTEST

The Colgate-Palmolive-Peet Co. announces a contest in which prizes will be given to the persons who write the best letters concerning the use of Palmolive soap. Full details of this contest have appeared in the daily newspapers and national magazines.

Processing Fast Shades on

Bone Material

By **ERSKINE L. BARRIE**

THE chief difficulty encountered in coloring bone material such as chess and other game counters, buttons, horn handles for umbrellas and walking sticks, ornamental vases and similar bric-a-brac of this type, etc., consists in obtaining good penetration of the dye. It is an unfortunate fact that certain acid and basic dyes of poor fastness to light will penetrate bone material better than some of the faster colors. Where penetration is too shallow, bone articles subjected to much handling like chess and draughtsmen, umbrella and walking stick handles and so on, soon disclose unsightly light places where the superficial film of coloring matter has worn off.

Bone material is commonly dyed in a nested copper kettle, the inner container which carries the stock being perforated with small holes for the circulation of the liquor. The container can be lifted from the outer casing when it is desired to examine the stock during processing. Coloring of bone material is usually performed before it is polished, as treatment in hot liquor would roughen the surface of polished goods. When small articles like buttons, electric bell and light switch press-plungers, ivory sectors for inlay and marqueterie designs and so forth are to be colored, handling of the stock is facilitated by processing it in bags of linen net, each bag having a capacity of about 8 ozs. of stock.

It is customary to boil-off bone material in clean water before coloring it. If the stock contains traces of oil or grease acquired during turning and fret-cutting of ornamental pieces, a small amount of pearl ash is put into the boil-off bath in order to emulsify the fatty substance. It is well to be sparing in the use of the alkali because the employment of an excessive amount will turn the bone a yellowish color. The use of soap for boiling-off is also apt to bring about this yellow discoloration in the stock; moreover, the presence of residual soap during coloring of the bone material will hinder penetration. The usual duration of the boil-off is from fifteen to sixty minutes, according to the size of the pieces in the stock and the kind of bone. Antler and tusk material is harder and less porous than stock manufactured from sawn bone of bovine origin.

When the stock has been taken out of the boil-off kettle, it is plunged into the boiling dyebath, which is already fully charged with the appropriate dyestuff. Boiling proceeds for 30 to 60 minutes and then the stock is allowed to steep in the cooling bath for several hours in order to encourage penetration. It is not always advisable to process thin pieces made of horn at boiling temperature for longer than a few minutes, because of the risk of distorted material through softening of the structure in the hot liquor.

The following dyes may be employed for processing fast-to-light colors on bone material. Afterchrome Black of the PV type; Alizarine Brilliant Green G; Cloth Fast Yellow R; Eriochrome Red G; Erio Fast Brilliant Blue 3R; Radio Brown B; Cutch Extract; Lockwood Extract. Afterchrome Black is applied to bone material in a boiling bath containing 1 per cent of acetic acid, 30%. After processing for half-an-hour, 1 per cent of sulfuric acid 168 deg. Tw. is added and boiling is continued for a further half hour. The stock is then allowed to steep in the cooling bath for some hours, after which it is plunged into a fresh bath containing a boiling solution of bichromate of potash, the amount employed being from 1 to 2 per cent. After 15 minutes processing at the boil, steam is turned off and the stock is left to steep for a further period of fifteen minutes and then it is lifted and rinsed in warm water.

Alizarine Brilliant Green G yields fine blue-green hues of high fastness to light on clean white bone stock; when this color is used on discolored stock, or the darker sorts of horn material, the shade which ensues is a bottle-green color. Alizarine Brilliant Green G has good affinity for bone when applied in a boiling neutral bath. For deep shades with this dyestuff, an addition of 1 per cent of acetic acid should be made to the bath after processing neutral for half-an-hour. Cloth Fast Yellow R also possess good affinity for bone in neutral liquor. Deep hues may be processed with an addition of acetic acid, this to be put in when the bath has boiled for half-an-hour. Eriochrome Red G yields rich red on bone stock. Dyeing should be commenced with the addition of 1 per cent of acetic acid and when the bath has boiled for half-an-hour,

1 to 2 per cent of bichrome may be put in. If the stock is hard tusk, boiling should be kept up for an hour before the bichrome is used. Erio Fast Brilliant Blue 3R produces a lively and very durable reddish-violet color on clean white bone material. This dyestuff has very good affinity for bone in a neutral bath. When processing a full shade, an addition of 1 per cent of acetic acid may be made after the bath has boiled one hour.

Radio Brown B is a useful dyestuff for processing light or dark brown hues of first-rate fastness to light on bone stock. The affinity in a neutral bath is not good, hence an addition of acetic acid may be used at the commencement of dyeing. After the bath has been boiled for about half-an-hour, the color may be exhausted by an addition of 1 per cent of sulfuric acid.

Cutch extract is an old favorite amongst bone dyes. This substance yields olive-gray to rich brown hues on bone, the shade depending on the processing method adopted. To produce olive-gray on bone stock, the material is boiled for thirty minutes in a bath containing 10 to 20 per cent of dry cutch extract and 1 to 2 per cent of acetic acid. Steam is then cut off and the stock allowed to feed in the cooling bath for eight to ten hours. The material is then put into a net bag and suspended in an empty barrel into which steam is blown for ten minutes. The jet of steam must not impinge directly upon the stock. Oxidation of the cutch which has been absorbed is then completed by exposing the bone pieces to the air while they are spread out in shallow trays. In order to develop the olive-gray coloration, the stock is plunged into a boiling bath containing 2 to 5 per cent of green copperas. Steam is cut off after the material has boiled for fifteen minutes, after which the stock is left to steep for half-an-hour and then rinsed. The olive-gray hue produced in this manner has long been a popular color for the bone platings on pocket knives. If it is desired to process orange-brown or deep reddish-brown with cutch, development of the color is done with bichrome and copper sulfate instead of green copperas. When deep colors are being processed on bone material with cutch, or other natural coloring matters, it is usually necessary to remove the film of loose color and resinous impurities which forms on the surface of the bone during processing. If this film is not cleaned off, it clogs the pores in the bone and hinders development of the final color during after-treatment with the metallic salts. In order to cleanse the stock, the pieces are put in the loose condition into a tumbler apparatus containing a thin paste of sawdust and water, or preferably cow dung and water. When the device is set into motion, the movement of the stock in contact with the sawdust etc., cleanses away the film.

Logwood extract is sometimes combined with cutch for the purpose of modifying the tone of the latter. Logwood extract is also used for deep black on bone articles, the process consisting in boiling the stock in a solution of Logwood extract, followed by the oxidation of the hematine by steaming and exposure to the atmosphere. After the material has been freed from film in the tumbler apparatus, the black color is developed in a boiling bath containing copper sulfate and green copperas. A black of this kind is not as fast to light as afterchrome black, but penetration is frequently better than in the other instance.

• LUNCHEON FOR CORNELL CHEMISTS

All Cornell chemists, whether members of the American Chemical Society or not, are urged to attend the Cornell Group Luncheon Meeting, which will be a feature of the spring meeting of the American Chemical Society.

The date assigned to Cornell is April 24th, and the luncheon will be held at one of the convention hotels in New York City. August Merz, vice-president of the Calco Chemical Company, Bound Brook, N. J., is in charge of arrangements, and will appreciate hearing from Cornell chemists not already on his list who may be able to attend the luncheon.

• NORTH CAROLINA STATE COLLEGE TEXTILE SCHOOL (on the air)

Last week students from the North Carolina State College Textile School gave a fifteen-minute broadcast over station WPTF. The broadcast was sponsored by the Honor Scholarship Soc. "Pine Burr," taking the form of a dialogue, outlining the whole process of converting raw cotton into a finely dyed and finished fabric. The relation and importance of the textile school in present development of the textile industry was stressed.

The broadcast was conduced by Aaron Epstein, President of the Pine Burr Society; M. C. Hunter, a student member of the A. A. T. C.C., and J. E. Shaw, another student in the Textile Department.

• LOWELL TEXTILE ALUMNI

The New York Chapter of the Alumni Association of the Lowell Textile Institute will hold its final meeting of the season on Friday evening, April 12th, at the Old Timer's Grill, 7 East 40th Street. Dinner will be served at 7 P. M.

Charles H. Eames, president of the Institute, will be present and will address the gathering. Election of officers for the next season will take place and there will be discussion concerning the Annual Alumni Day at Lowell, Massachusetts.

• KNITTING ARTS EXHIBITION

The Thirty-first Annual Knitting Arts Exhibition, held under the auspices of the National Association of Hosiery Manufacturers, will be held in the Commercial Museum, Philadelphia, Pa., during the week of April 22nd. Knitting, dyeing and drying machinery, together with allied products of interest to the knitting field will comprise the exhibits. Association meetings will be held during the week.

Technical Notes from Foreign Sources

New Analytical Methods for Weighted Silk

Dr. Weltzien and Dr. A. Schotte—Monats. f. Seide u. Kunst-Seide, 38, 243 (1933).—The second part of the paper (the first part recently reviewed in these columns). This second part deals with the swelling of weighted silk in cupro-ammonium reagent.

The question as to whether weighting silk increases the volume of the fiber, and whether it does so proportionately, if at all, has been studied by Heermann, Heermann and Herzog, and Pohl. Their work considered the relative diameters of the fibers, and the area of cross-sections of the fibers, in the dry state; and the conclusion was reached that a considerable increase in volume of the fiber does take place in weighting. The authors also pointed out that mere measurement of diameter of the fiber would not give worth-while results, owing to the infinite variation in this factor in a single filament; that a study of the area of cross-sections was the only decisive method of study.

The present authors have considered the question of the swelling of weighted silk fibers in cupro-ammonium reagent. It being known that unweighted silk dissolves completely in this reagent, the first point raised was that of the behavior of weighted silk in it. It appeared that weighted silk does dissolve in cupro-ammonium reagent, but not completely, but swells more or less strongly, and disintegrates into fibrillar fragments under slight pressure (e.g., by moving the cover-glass gently to and fro over the mounted specimen upon the slide). Measurement of the degree of swelling, based upon the diameter of the fiber, did not appear promising, as a given fiber swells non-uniformly (it was supposed at first to be so). It occurred to the authors, however, that this irregular swelling might be due only to local exhaustion of the cupro-ammonium reagent, at this or that point along the fiber, so little of the reagent being available, in the space between the cover-glass and the slide. They therefore, subjected fibers to a thorough swelling for 5-10 minutes in plenty of the reagent, in a small, covered dish, before mounting them in fresh reagent, and found that, given this opportunity to swell ad libitum, the fibers did swell to a remarkable degree of uniformity. The earlier irregularities encountered by previous workers were, therefore, due to incomplete swelling, i.e., proper experimental conditions had not been maintained.

Heermann, Herzog, and Pohl stated, as a result of their studies, that exact measurement of the increase in volume by weighting could be made only by determining the areas of cross-section of the fiber, as the irregular swelling of the fiber made diametric measurements valueless, though they admitted that, for comparative purposes, the diameters of the fibers could be considered. But the present work shows that diametric measurements can be used perfectly well, with the uniform and maximum swelling produced by the new procedure.

The authors find that the degree of swelling depends upon the amount of weighting, in that, as the amount of weighting increases, the degree of swelling decreases, and very strongly so (swelling, that is, in cupro-ammonium reagent). A considerable range of samples, of various degrees of weighting, and of age, was examined.

With so variable a substance as natural silk, it would be expected that strictly quantitative comparative figures could not be obtained. The authors, however, have been able to establish groups, in one or another of which a given fiber under examination could be located decisively.

It is possible, by using the new method of swelling, and bearing in mind the inverse relation between weighting and swelling, to detect in finished goods any portions which have not been properly weighted, whether from defective impregnation in the general sense, or from mechanical interference by deposition of less permeable solids upon the fiber during normal weighting. Of course, such indications do not make it possible to reweight the goods properly; they simply call attention to the fact that the weighting is not being carried out properly—therefore a very valuable means of control.

Skin Troubles from Dyed Textiles, etc.

Dr. Karin Schulze—Monats. f. Seide u. Kunst-Seide 38, 247 (1933).—Cases come to light now and then, in which inflammation or some other morbid condition of the skin is ascribed by physicians to contact with dyed fabrics, furs, felt hats, etc. This accusation has been altogether too frequent, as some such results have been later proven to be due only to hyper-sensitiveness toward, perhaps, even only the substance of the colored material itself, without its having been necessary to ascribe any poisonous properties to the dyestuff or substances possibly contained in it, with which the article was dyed. Furs, perhaps, are most often the commonly blamed cause of skin troubles.

Physiological investigations have shown that there are very few, comparatively, of the enormous number of dyestuffs known, which produce eczematous symptoms, and of these most only under very special circumstances. Many of these cases can be responsible for skin trouble only at some point during their manufacture of the dyestuff, which carries the question back behind the dyestuff, to one or another of the intermediates employed. It should be noticed also, in this connection, that skin irritation is produced even in these cases by contact with a

relatively large amount of the pure substance, a very different matter from the occasional light contact of a fabric, etc., dyed with the dyestuff. Koelsch, in a careful study of the question, has established the fact that dyestuffs derived from anthraquinone (alizarine and Indanthrene groups), or quinoline, or the benzidine group, or most azo dyestuffs which contain the naphthalene ring, do not produce any eczematous irritation at all, under any circumstances, as far as known. Weyl and White agree with him that there are very few azo dyestuffs indeed which can cause such trouble (few, that is, again considering the very great number of dyestuffs known).

Koelsch has found that the following amino-azo dyestuffs are eczematogens; Aniline Yellow (amino-azobenzene), Chrysoidine, Butter Yellow, Fast Yellow (Aniline Yellow sulfonated), Metanil Yellow, Bismarck Brown, Vesuvine. Some of the ice colors belonging to the azo group are also occasionally troublesome; Koelsch and Mayer mention dyeings of Para Red and Ice Black as causing eczema (surely the term is employed rather loosely?). There is a feeling that trouble caused by such dyeings may be due to presence of diazo salts, for some reason not coupled (used perhaps in excessive quantities) and either surprisingly stable for longer periods than would be expected, under the condition of diffusion through the fiber, or else causing trouble in the shape of their decomposition-products. Hannay also cites the diazo salts of Fast Scarlet G and R bases (a nitro-toluidine and a nitro-anisidine) as specially active "Noxenes". Cox mentions in the same way stabilized diazo-nitro-amines used in Naphthol printings. In several of these cases, however, the present author remarks that the inflammation caused by the dyeings was due not to the diazo-salts, but more evidently to the naphthols used, and remaining in the free state in the dyed goods. Koelsch notes that beta-naphthol does provoke dermatitis in some cases (though much used in medicine to allay certain irritations of the skin), and Hannay states that the Naphthol AS components also bear this bad reputation.

Of the triphenyl-methane group of dyestuffs, in the general sense, the following dyestuffs, according to Koelsch, have occasionally been thought to have caused dermatitis; Malachite and Brilliant Greens, Fuchsine, Rubine, Acid Fuchsine, Methyl Violet, Spirit and Water-Blues. Sachs also mentions Crystal Violet and Victoria Blue as strongly irritating. (It should be noticed that this list comprises practically all of the dyestuffs of this group which are most used, so that there may simply be much more evidence of their suspicious nature, because there are fewer cases of the less used colors available). Koelsch also mentions Erythrosine and Phloxine, of the phthalein group, as irritants; but these fluorescent dyestuffs probably are not toxic of themselves, but act photodynamically; i.e., they seem to increase the sensitivity of the skin to light, which results in irritation, not of a pathological nature. (It seems quite as possible to us, in view of the hypothetical nature of the suggestion just made, that the dyestuffs do not have any direct action upon the sensitivity of the skin, but that they so alter the transmitted light rays that they lie in a wave-length range which will produce a heightened action upon the skin. There is room for an interesting study of this possibility.)

Of the quinone-imides, and related groups, the Safranines are suspicious. Aniline Black is perhaps the one dyestuff best known to be irritating. Of other dyestuffs or dyeings which are certainly closely related to the quinone-imines, produced by oxidation of amino-compounds, several are under heavy suspicion, in some cases amounting to certainty. The so-called Ursol or Nako dyestuffs, the Furreins and Furroles, which are largely employed for the dyeing of browns and blacks of furs and felts, and at times, we regret to say, for the dyeing of human hair in the living state, in the vain hope of deceiving one's acquaintances ("Juvenia" and "Juvenil" dyestuffs, and such trade appellations), are the worst offenders of all. They are characteristically likely to produce severe dermatitis, if the skin is at all sensitive. Specified examples of this group are Ursol D (Nako Brown, Furrein D), which comprise such irritants as p-phenylene-diamine (this substance is being much used now-a-days as a component of fine-grain developers for the films used in the popular miniature cameras, and one is warned to wear rubber gloves while working with it), m-phenylene-diamine, the three toluylene-diamines, p-amino-acetanilide; Ursol P (Nako Brown) or p-amino-phenol; Fuscamine D, or m-amino-phenol; Ursol GG, or o-amino-phenol, Metol (the same substance used as a photographic developer, and responsible for many severe and obstinate cases of dermatitis of the finger-tips); also 2-4-diaminophenetole and p-amino-dimethyl-aniline; and Diphenyl Black Base I, or p-amino-diphenylamine, also p-p-diamino-diphenylamine, 1-4-naphthylene-diamine, and dianisidine, well known as a nasal irritant.

Ursol D (p-phenylene-diamine may perhaps stand as the type of compounds of this group) seems to be the substance which has caused most complaints, as far as definite records go; it has therefore been given special study in the effort to determine which of the dyestuffs derived from it by oxidation may be held responsible for the difficulty. Koelsch and Mayer independently consider that the intermediate oxidation product, the very poisonous quinone-diimine, from which, through polymerization, the final dyestuff forms, is the substance which acts powerfully as a skin irritant. According to Erdmann, the final dyestuff is without action upon the skin. Also, the three-ring compound, the condensation-product, "Bandrowski's Base", formed from p-phenylene-diamine by cautious oxidation, is without action upon the skin, though two of the three rings contain the dangerous p-diamine grouping, and the third ring, the middle one, contains the quinone-diimine grouping. Probably the

(Continued on page 198)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

APRIL 8, 1935

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Proceedings of the American Association of Textile Chemists and Colorists

Carbonizing of Wool*

By JAMES GILET†

THE carbonizing of wool has been my profession for the last forty years. In Verviers, Belgium, the manufacture of cloth more than a hundred years ago was done mostly by hand-work, and crude machinery. Wool was washed by hand and dried in the fields, this wool containing some burrs which had to be picked out by hand.

The history of wool carbonizing has not been recorded in book form, at least not to my knowledge, and my talk consists of my practical experience and from what one man, a carbonizing machinery builder, has told me some forty years ago. It seems that a man by the name of Romain, I believe, a good many years ago was experimenting in his house with chemicals and wool; a bucket containing a solution of sulfuric acid was on the floor, near a bench on which was a bunch of burry, washed wool, which the man inadvertently and unknowingly pushed off the bench and into the bucket of acid solution. After a while, he thought of the wool, which he found steeped in the liquid, which he squeezed out, and put the wool to dry on a tray in an ordinary kitchen stove oven. When it was thoroughly dry, he noticed that the burrs and shives had become blackened and by pressure between the fingers were rather easily crumbled. The wool carbonizing process was thus discovered by accident, like many other inventions and processes.

As I remember, the first means used for wool carbonizing consisted of rooms of various sizes, whose floors had been replaced with heavy wire netting, and rows of steam-pipes installed underneath the netting, over which the acidified wool was spread and turned over several times until the burrs, shives, etc., had turned black by the heat rising from the steam-heated pipes. An improvement was then brought about by replacing the rooms and screens with steel and cast iron chambers built in sections; each section having five or six metallic screened drawers on which the acidified wool was spread by two men, and the heat from steam-pipes the length of the chamber under each drawer, rising through the layers of wool. This way of carbonizing, which like the first, was affecting the color and strength of the wool, was improved upon by placing the steam-pipes in what is called an aero, or coil house, at one end of the chamber instead of beneath the drawers, with large fan or blower forcing air around the steam-heated pipes, and this air was forced under each section of drawers where a controlling damper was placed.

Then an Englishman, living in Verviers, by the name of Condrexon, had the idea to build a machine, consisting of cast iron frame, fire-brick walls, three wide conveyors and the hot air distribution, by forcing it and baffling it from the bottom up through the layers of acidified wool; each conveyor was operated independently by one man, who also spread the wool as evenly as possible on a wooden slatted apron and each time that the man operated a lever, the wool on the apron entered the machine and a corresponding quantity dropped carbonized on the floor at the other end. The same operation was gone through with each of the three conveyors.

The next improvement consisted in using the same machine, but in mechanically driving the three conveyors automatically and continuously, so that there was no more stoppage, the acidified wool being spread continuously on the apron, entering the machine, being carried the length of it on the top conveyor, then dropping on the second, then on the third and finally coming out of the machine automatically.

The modern carbonizing machine is an improvement over the latter, with various ways of hot air distribution and with from one to five conveyors. There are some other makes of machines for carbonizing wool, some upright, like large chimneys with 5, 7, 9 metallic screened cylinders revolving and dropping the wool from the top cylinder to the next one below and so forth; other machines have metallic screened plates being lowered slowly and dropping the carbonized wool at the bottom. Other machines are shaped like large cylinders with compartments in which the wool is placed by hand and all these machines have the aero mentioned above and big fans or blowers for the heated air circulation.

When the wool carbonizing process was discovered, as related previously, some means of crushing the burrs had to be found and at first this was done by laying the hot carbonized wool on wood slatted tables and men pounding

*Presented at meeting of the Rhode Island Section, October 26th, 1934.

†Gilet Carbonizing Co., Lowell, Mass.

the burrs with wooden mallets, the burrs reduced to carbon dropping between the slats into boxes. Then a machinery builder constructed a machine with, first one pair of iron fluted rolls which proved so successful, that now multiple double roll crushers are used. After crushing, the wool was dusted, at first with willows, then with automatic dusters, the wool entering at one end and coming out at the other.

Next is the removal of the acid and dirt left in the wool by passing it through a neutralizing machine which is the same as a washing or scouring machine, composed of three, four, five or six bowls of various lengths and widths, through which the wool is passed automatically and squeezed at the end of each bowl, then free from dirt and acid the wool is dried on a machine similar to the carbonizer.

The complete modern carbonizing process of wool, such as the sample I am sending amongst you, consists of:

First—Sorting for the various qualities, and elimination of defective parts.

Second—Washing or scouring out of the grease and dirt.

Third—Steeping in a solution of water and sulfuric acid at various strengths.

Fourth—Hydro-extracting or pressing of the excess acid water.

Fifth—Drying in an automatic machine having one or more conveyors and one or two compartments.

Sixth—Carbonizing in the same machine or in a second connected, having also one or more conveyors.

Seventh—Crushing of the carbonized burrs and other vegetable matter.

Eighth—Dusting of the carbon and dirt left in the wool.

Ninth—Neutralizing for the removal of acid and remaining dirt.

Tenth—Drying and finally bagging or baling up.

Wool, which years ago, because of its very burry condition, was selling in the markets at far lower prices than free from burrs wool, was made available to the manufacturers of this country, because of the carbonizing process, which, at the time of my arrival in this country in 1897, was to my knowledge done for the trade by one firm only. Since then several more have established commission wool scouring and carbonizing plants in this country, so that now there are over twenty mills doing that work, and many manufacturers have installed their own scouring and some carbonizing equipment, either for raw stock or cloth.

In Verviers and vicinity (Belgium), there are over thirty commission wool scouring and carbonizing plants, and their products are used all over the world by woolen, wool felt, wool felt hat and other manufacturers of wool articles.

In wool carbonizing, three processes are used in this country:

First—The sulfuric acid, which, in my opinion, is the best.

Second—The chloride of aluminum, which some knit goods manufacturers prefer.

Third—The dry or hydrochloric acid vapors process.

DISCUSSION

Q. Could you tell us something about the new process of removing burrs by freezing?

A. I have been at the school (Lowell Textile Institute) and have seen some samples which looked very good, although I was sceptical about it. The professor in charge told me that they were going to put through a 20,000-pound lot of wool. I spoke to someone else, and he told me that something was not quite right with the feed of the wool inside the machine. This has since been corrected.

Q. How about the dust?

A. There is no dust, because the grease is so hard. This process consists of a freezing machine and one conveyor machine, similar to a wool dryer, and from there the wool passes to a duster. I have not seen the new duster yet.

Q. Do you know at what temperature they freeze?

A. 40° below zero.

Q. In comparing those three processes of carbonizing, those which use heat and the cold process, which process is going to be to the best advantage of the wool in regard to whiteness, softness, etc.?

A. I have only seen samples of the wool done by the cold process, so I can hardly answer that question. The difference between the cold process and the others will probably be a question of cost.

Q. You mention that after soaking, you extract. The acid coming from the extractor, do you use it again?

A. Yes.

CALENDAR OF COMING EVENTS

Meeting, New York Section, Paterson, N. J., April 26, 1935

* * * *

Spring Meeting, Piedmont Section, Poinsett Hotel, Greneville, S. C., May 4, 1935.

Proceedings of the American Association of Textile Chemists and Colorists

The Amino Nitrogen Contents of Wool and Collagen*

By MILTON HARRIS** and JOSEPH R. KANAGY†

CONTENTS

I. Introduction
II. Materials and Methods
III. Experimental
IV. Discussion
V. Conclusion

ABSTRACT

When wool, collagen and arginine were treated with nitrous acid, increasing amounts of nitrogen were evolved with time. The continued evolution of nitrogen was due to the action of nitrous acid on the guanidine nuclei of these materials.

A new method for the determination of the arginine content of a protein is given. The method is based on the relative rates of evolution of nitrogen from the guanidine nuclei in a protein and in arginine.

Evidence is presented to show that the action of nitrous acid on the guanidine nucleus is different from its action on a free amino group. The free amino nitrogen contents of wool and collagen were calculated by subtracting from the total nitrogen evolved that portion of nitrogen which came from the guanidine nuclei. The values obtained for the percentages of the total nitrogen as amino nitrogen are 2.53 for wool and 2.77 for collagen.

I. INTRODUCTION

THE free amino groups in wool and collagen have been related to the combination of these materials with acids, dyes and tannins by various investigators. Trotman[1], and Benz and Farrell[2] claimed that deamination of wool had little effect on the affinity of wool for acid dyes, but Speakman and Stott[3] later showed that the affinity of untreated wool was much higher than that of deaminated wool. Speakman and Hirst[4] attempted to account for the acid adsorbed by wool in terms of its free amino nitrogen and histidine contents, but later stated[3] that wool did not combine with acid solely through the simple amino groups. Thomas and Foster[27] worked with deaminated collagen and showed that the absence of the free amino groups greatly decreased the ability of collagen to combine with tanning material.

The method these investigators employed for the determination of the free amino groups is based on the reaction between these groups and nitrous acid, whereby the nitrogen of the amino group is liberated and the amino group is replaced by a hydroxyl group according to the following scheme.

(I) $$R{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}NH_2 + HNO_2 \rightarrow R{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}OH + H_2O + N_2$$

The values they obtained for the amino nitrogen contents varied greatly. The results of this present investigation show that their values do not necessarily represent the true amino nitrogen content, and were dependent on the conditions under which their determinations were made. Owing to these discrepancies their attempts to relate the free amino nitrogen to chemical combination were solely of a qualitative nature.

II. MATERIALS AND METHODS

A number of methods are now available for the determination of amino nitrogen. The advantages and limitations of each have been compared and discussed by a large number of workers[5, 6]. While none of the methods is entirely satisfactory for the determination of amino nitrogen in complex mixtures, the method of Van Slyke, which is based on the reaction in equation (I) appears to be the best for estimating the free amino nitrogen in native proteins.

In this work a Van Slyke macro-apparatus[7] was used. Since the amounts of amino nitrogen obtained were small, a 3-ml. gas burette was substituted for the standard 40-ml. burette. The nitrous acid was obtained by the interaction of equivalent quantities of sodium nitrite and acetic acid. The apparatus was calibrated to deliver 9.72 ml. of glacial acetic acid and 38.88 ml. of a 30 per cent solution of sodium nitrite into the reaction vessel. After the air in the reaction vessel was displaced by nitric oxide, formed by the decomposition of the nitrous acid, all but 5 ml. of the nitrous acid was forced out of the reaction vessel. The reaction vessel is calibrated to hold 20 ml. of nitrous acid. However, it was found advantageous to dilute the nitrous acid solution. The dilute solution evolved much less nitric oxide, gave more reproducible blanks and caused less frothing. The nitrous acid remaining in the vessel was diluted with 10 ml. of water and then 10 ml. of the solution to be analyzed was introduced.

At different intervals of time, the gas evolved was run into a Hempel pipette containing an alkaline permanganate solution, which absorbed the nitric oxide. The volume of nitrogen was measured and the temperature and pressure were noted. The weight of a given volume of nitrogen at a known temperature and pressure was read

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**Research Associate at the National Bureau of Standards from the American Association of Textile Chemists and Colorists. The work on wool was made possible by a grant from the Textile Foundation, Incorporated.

†Junior Chemist, National Bureau of Standards.

directly from a table prepared by Van Slyke[7]. The values obtained were corrected for the amount of nitrogen obtained in blank determinations which were made for each time interval.

The experimental errors were minimized by keeping the stopcocks well greased, changing the permanganate solutions after every five or six runs, using freshly-prepared and more dilute solutions of nitrous acid, and making blank determinations under the identical conditions of the original determinations.

One of the sources of error in amino nitrogen determinations by the Van Slyke method occurs in making a correction for the amount of nitrogen evolved by the spontaneous decomposition of the nitrous acid itself. Since the amount of free amino nitrogen present in native proteins is very small, it is obvious that much care must be exercised in making such corrections. For a given time of reaction, the size of the blank depends on the age of the sodium nitrite solution, and the rate of evolution of the gas. The latter, in turn, depends on the speed of shaking and on the nature of the material being analyzed. For example, suspended particles cause a more rapid evolution of gas than materials in true solution. The effects of the various factors are illustrated in Table 1.

Table 1

The Effect of Various Factors on the Volume of Nitrogen Obtained in Blank Determinations.

Blank	*Time of Reaction* Minutes	*Age of $NaNO_2$ Solution*	*Volume of Gas Evolved** ml.	*Volume of Nitrogen* ml.
Water	5	1 hr.	75	.37
Water	5	24 hrs.	75	.43
Water	5	3 days	75	.48
Water	5	7 days	75	.49
Water	5	7 days	125	.55
Cellulose	5	1 hr.	75	.43
Water	15	1 hr.	85	.42
Cellulose	15	1 hr.	85	.46
Water	30	1 hr.	100	.43
Cellulose	30	1 hr.	100	.48
	Hours			
Water	2	1 hr.	125	.51
Cellulose	2	1 hr.	125	.53
Water	20	1 hr.	150	.91
Cellulose	20	1 hr.	150	.90

*The volume of gas evolved was estimated and the values are accurate to about 5 ml.

The blank determinations were made both on 10-ml. portions of distilled water and on 10-ml. portions of a 1 percent suspension of powdered cellulose. The initial amounts of nitrogen evolved were higher when powdered cellulose was used than with water alone but they became about equal after 2 hours. In the subsequent determinations on the wool and collagen suspensions, the corrections applied were obtained on blanks containing about the same weights of cellulose as of the protein used. In all determinations the reaction vessel was shaken during the last 3 minutes.

The wool used was prepared from raw stock which had been extracted with alcohol and ether and washed with water. The clean fibers were ground in a pebble mill for 48 hours and the total nitrogen of the resulting powder was determined. The values were corrected for ash and moisture.

Standard hide powder, American Leather Chemists Association 1933, prepared in the same manner as the wool, was used for the determinations on collagen.

The suspensions were prepared by shaking approximately 1-g. samples of the powder (particle size 0.3 to 2.0) in 100 ml. of water. A 10-ml. aliquot of the suspension was measured in the graduated cylinder of the Van Slyke apparatus and run into a Kjeldahl flask for determination of total nitrogen. Another 10-ml. aliquot was then measured in the same cylinder and run into the Van Slyke apparatus for determination of amino nitrogen.

The glycine and arginine hydrochloride were from the Eastman Kodak Company.

III. EXPERIMENTAL

While it is known that the alpha-amino groups of the individual amino acids react completely with nitrous acid in 5 to 10 minutes, the time required for the amino nitrogen in proteins may be much longer. As a preliminary investigation, the evolution of amino nitrogen from glycine when treated with nitrous acid for different lengths of time was determined. The rates of evolution of nitrogen from the nitrous acid alone and from the nitrous acid plus the glycine are shown in Figure 1. Since the curves are parallel, it is obvious that the increasing amounts of nitrogen, obtained by prolonging the time of reaction come from the nitrous acid itself. The amino nitrogen content of glycine at any time is obtained by subtracting the values on the lower curve from the corresponding values on the upper curve. These results are given in Table 2. The high values obtained are in accord with those found by Van Slyke[8] and Levene and Van Slyke[9] who obtained values of 103 to 107 percent of the total nitrogen of glycine as amino nitrogen. The anomalous results appear to be independent of time and to depend on some specific reaction of the glycine or its reaction product with nitrous acid. Van Slyke analyses of alanine gave values of 99.3 to 100.5 percent of the total nitrogen as amino nitrogen.

When 1 percent suspensions of powdered wool and collagen were treated with nitrous acid for different lengths of time and the necessary corrections for blank determinations applied, the values obtained were not constant as in the case of the mono-amino acids, but in-

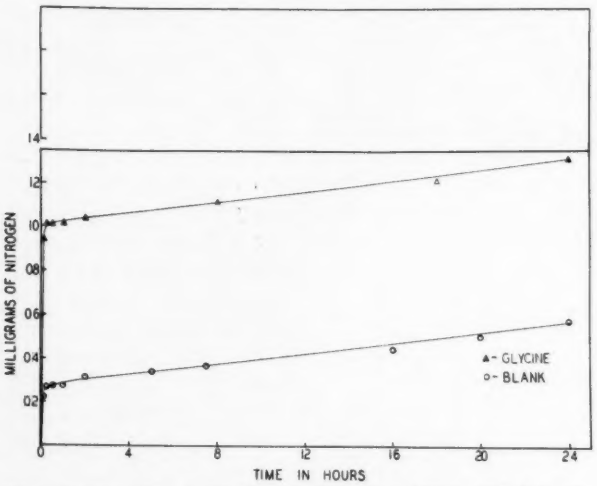


Fig. 1—Relative rates of evolution of nitrogen from nitrous acid alone and from nitrous acid and glycine.

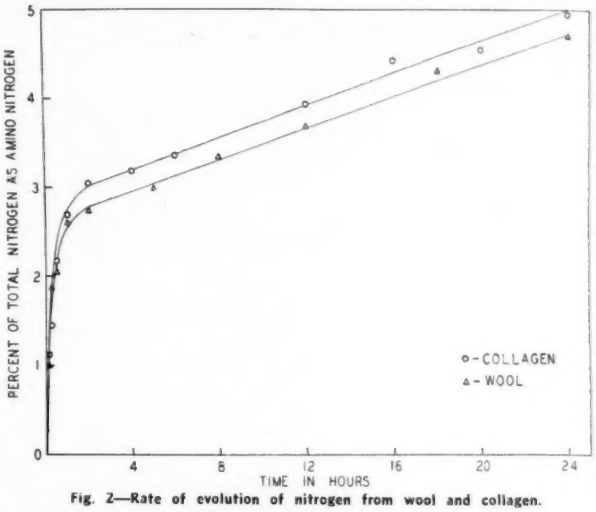


Fig. 2—Rate of evolution of nitrogen from wool and collagen.

creased with increase in time of reaction. The results are shown in Figure 2. In the case of wool, this increase in the amount of nitrogen evolved with time had been previously noted by Meunier and Rey[10] and by Speakman and Hirst[4].

Table 2

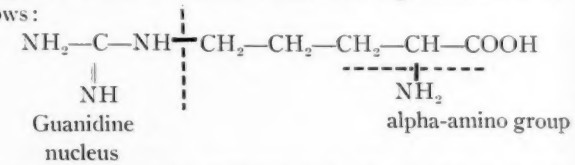
The Amino Nitrogen Content of Glycine.

Time Minutes	*Total Nitrogen as Amino Nitrogen* Per Cent
5	99.2
15	105.5
30	103.6
Hours	
1	103.2
2	102.5
8	106.3
18	105.6
24	105.7

Since the pH of the nitrous acid solutions was about 4, there was little reason to believe that the increased evolution of nitrogen was due to a hydrolysis occurring during the reaction. The absence of hydrolysis was demonstrated by treating wool and collagen for periods of 24 and 48 hours with sodium acetate-acetic acid solutions containing acid and salt in amounts approximately equivalent and at nearly the same pH as those found in the nitrous acid solutions. The specimens thus treated showed no measurable increase in amino nitrogen content by the Van Slyke method.

In the absence of any hydrolysis it seemed probable that the increasing amounts of nitrogen obtained might be formed by the slow interaction of nitrous acid with a nitrogen-containing group other than an amino group.

Although the Van Slyke method has been shown to give high amino-nitrogen values for a number of the individual amino acids[8, 9], the only amino acid present in wool and collagen in appreciable amounts, which is known to give off increasing amounts of nitrogen with time is arginine[11]. Its structural formula is represented as follows:



It seemed logical therefore to study the rate of evolution of nitrogen from this amino-acid under conditions identical with those used for wool and collagen. The results are shown in Figure 3. Since arginine contains 4 nitrogen atoms, it is obvious that an amount of nitrogen equivalent to 1 atom is evolved during the first 5 minutes of reaction. This nitrogen comes from the alpha-amino group. The nitrogen subsequently evolved is formed by the action of nitrous acid on the guanidine nucleus.

The exact structure of guanidine or the guanidine nucleus is not known but most investigators agree that the NH_2 group, if one is present, is not a true free amino group. Their evidence will be presented later. That the nitrogen evolved by the interaction of nitrous acid with the guanidine nucleus was not produced in the same manner as nitrogen obtained by the action of nitrous acid on a free amino group as further demonstrated by the following experiments. Tenth-gram portions of arginine hydrochloride were introduced into Kjeldahl flasks and 25 ml. of a nitrous acid solution of the same concentration as used previously in the Van Slyke analyses was added to each. After the reaction had proceeded for a definite interval of time, the solution was diluted to about 200 ml. an excess of magnesium oxide added and the

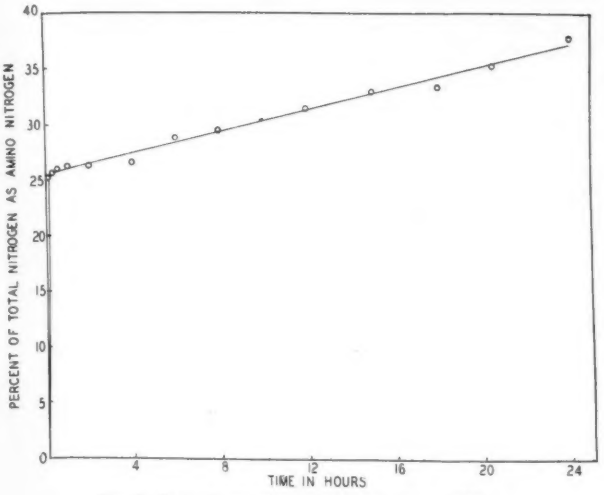


Fig. 3—Rate of evolution of nitrogen from arginine.

amount of ammonia in the solution was distilled off and determined. For controls, 0.1-g. portions of arginine hydrochloride were treated with acetic acid and 0.1-g. portions of glycine were treated with nitrous acid in the same manner. The results are recorded in Table 3. The

Table 3

The Effect of the Continued Action of Nitrous Acid on Arginine. The Values given are in Milligrams per Gram of Amino Acid.

	Amino Nitrogen		
Time Hours	*Glycine Treated with HNO_2* mg.	*Arginine Treated with HNO_2* mg.	*Arginine Treated with Acetic Acid* mg.
3	0.5	21.4	0.7
6	0.6	25.1	0.6
24	0.8	20.3	0.8
48	0.9	12.3	1.2
72	..	6.6	1.3

reactions of nitrous acid with the guanidine nucleus are complicated and it is not desired to place any emphasis on these results as a possible explanation of the mechanism of the reactions. However, the data show that ammonia is a product of at least one of the reactions, and that the amount of ammonia present in the solutions reaches a maximum and then decreases with time. This is to be expected since ammonia reacts with nitrous acid to form ammonium nitrite and the latter decomposes with the liberation of nitrogen according to the following reactions:

(II) $NH_4OH + HNO_2 \rightarrow H_2O + NH_4NO_2 \rightarrow 2H_2O + N_2 \uparrow$

IV. DISCUSSION

The similarity of the reaction of nitrous acid with arginine to its reaction with wool and collagen indicates that the continued evolution of nitrogen (as represented by the straight line portions of the curves in Figure 2) is due to the action of the nitrous acid on the guanidine nuclei of these proteins. If it is assumed that all of this portion of the total nitrogen evolved comes from the guanidine nucleus, then the fraction of the total nitrogen of the protein as arginine nitrogen is equal to the ratio of the slope of the curves for wool or collagen (Fig. 2) to the slope of the curve for arginine (Fig. 3). It is thus possible to calculate the arginine contents of these materials from the following equations:

$$A = \frac{(F_a)\ (N_p)}{(N_a)} \times 100 \qquad \text{(III)}$$

where:

A = the arginine content of the protein in per cent.
F_a = the fraction of the total nitrogen of the protein as arginine nitrogen.
N_p = the nitrogen content of the protein.
N_a = the nitrogen content of arginine.

$$F_a = S_p/S_a \qquad \text{(IV)}$$

where:

S_p = the slope of the straight line portion of the curve for proteins.
S_a = the slope of the straight line portions of the curve for arginine.

substituting (IV) in (III),

$$A = \frac{(S_p)\ \ (N_p)}{(S_a)\ \ (N_a)} \times 100 \qquad \text{(V)}$$

The slope of the curve for collagen is 0.0875, for wool 0.0865, and for arginine 0.488. The corresponding nitrogen contents are 17.40, 16.32, and 32.18 percent. Substituting these figures in equation (V), the arginine contents of the wool and collagen were found to be 9.0 and 9.7 percent, respectively.

By methods of isolation, Stewart and Rimington[12] and Vickery and Block[13] found 6.0 and 7.8 percents respectively of arginine in wool. Marston[14] employing indirect methods found 10.2 percent. The arginine content of collagen has been reported as 8.2 percent by Dakin[15] and as 7.62 by Fischer, Levene and Aders[16]. These values were also obtained by isolation of the amino acid. The separation of amino acids by isolation from protein hydrolysates is a long and tedious process, and, at best, cannot be carried out without the loss of a considerable portion of the material. The summation of the amino acids of most of the proteins analyzed accounts for only about 65 to 85 percent of the protein. In view of the fact that isolation methods for amino acids are known to give low results, the method described in this paper may be considered to give better values for the arginine contents of wool and collagen.

The amino nitrogen contents of wool and collagen were obtained by subtracting from the total nitrogen evolved that portion of the nitrogen evolved from the guanidine nucleus of the arginine in these materials. The arginine contents were those calculated in this paper. The calculations were made with the experimental values and are not points taken from the smooth curves. The results are recorded in Table 4. From the average values in Table 4 and the nitrogen contents of wool and col-

Table 4

The Amino Nitrogen Contents of Wool and Collagen. The Values given are in Milligrams per Gram of Protein.

Time Hours	*Wool* *Total Nitrogen Evolved* mg.	*Arginine Nitrogen* mg.	*Amino Nitrogen* mg.
2	4.48	0.38	4.10
5	4.89	0.85	4.04
8	5.46	1.30	4.16
12	5.96	1.88	4.08
18	6.96	2.52	4.44
24	7.66	3.68	3.98
			Ave... 4.13
	Collagen		
2	5.30	0.41	4.89
4	5.56	0.53	5.03
6	5.83	1.25	4.58
12	6.88	2.03	4.85
16	7.66	2.66	5.00
20	7.92	3.22	4.70
24	8.62	3.97	4.65
			Ave... 4.82

lagen, the percentages of the total nitrogen as amino nitrogen were found to be 2.53 and 2.77 respectively.

It is apparent from the above calculations that in this work the free amino groups have been considered to be only those that react with nitrous acid according to equation I. Bracewell[17] suggested that other free amino groups are present in the protein molecule but they are anomalous in that they do not react with nitrous acid. The investigations of Werner[18] showed, however, that anomalous amino groups have no real existence. Bancroft and Ridgway[19] summarized the work on the reactions of nitrous acid and guanidine. They found that various formulae have been assigned to the latter to account for its behavior but that the experimental data did not conclusively favor any one formula. From their own investigations they concluded that guanidine and pure nitrous acid did not react, that excess acid other than nitrous acid catalyzed the reaction*, and that the rate of evolution of nitrogen depended on the concentration of nitrous acid, the hydrogen ion concentration, and a specific effect due to the acid itself. Clark and Gillespie[20] showed that in the presence of sodium carbonate, benzenesulphonyl chloride combined only with the alpha-amino group in arginine. The evidence indicates that an amino group does not exist in guanidine, or, if one does exist, it does not function as a free amino group.

Whether or not the guanidine nucleus is considered to contain a free amino group, it is obvious that treating a native protein with nitrous acid for an arbitrary length of time will not necessarily give a value which represents the true amino nitrogen content of that protein. Meunier and Rey[10], on treating wool with nitrous acid for seven hours found that 5.7 mg. of nitrogen was evolved from each gram of material. They assumed this to be the content of free amino nitrogen. Speakman and Hirst[4] likewise treated wool for 24 hours and obtained values of 9.2 and 11.9 mg. of nitrogen per gram of wool. Subsequently Speakman and Stott[3] studied the action of three concentrations of nitrous acid on wool and stated: "It is evident that the amino nitrogen content of wool cannot be defined with any degree of precision. The rate of evolution of nitrogen depends to a striking extent on the concentration of nitrous acid * * * ." They also determined the acid-combining capacity of untreated and deaminated wool and found that the latter retained slightly more than half of its maximum combining capacity for hydrochloric acid. They concluded that the nitrogen liberated from wool could scarcely be derived solely from the arginine and lysine side-chains, and in view of a recent study of the action of nitrous acid on cystine[24] it seemed likely that part of the nitrogen was derived from the action of nitrous acid on the sulfur linkage. Lough and Lewis[24] in their studies of the action of nitrous acid on cystine found that "extra" nitrogen was obtained only when oxidation of sulfur to sulfate occurred. Recently an attempt[25] was made in this laboratory to oxidize the sulfur in wool to sulfate with bromine and hydrochloric acid. Even with such a strong oxidizing agent only very small amounts of sulfate were obtained in period of 24 and 48 hours. In view of this and the fact that the sulfur in wool has very different properties in general from the sulfur in cystine, it hardly seems justifiable to assume the formation of "extra" nitrogen.

The similarity of the behavior of the guanidine nucleus of the arginine in wool and collagen with that of the guanidine nucleus of arginine itself indicates that the former is free in the native protein. Since the guanidine group is a strong base and readily combines with acids, it should be possible to account for the acid taken up by wool and collagen by their free amino groups and guanidine nuclei. Bancroft and Ridgway[19] stated that guanidine is a mono-acid base, while Schmidt, Kirk and Appleman[21] determined the titration curve of arginine and found that arginine monohydrochloride combines with 1 equivalent of hydrochloric acid. On the basis of the amino groups and guanidine nuclei each combining with 1 equivalent of acid, the amounts of acid that will combine with wool and collagen have been calculated. The

*Acetic acid is always present in the Van Slyke procedure. It is apparent therefore that the slopes of the curves will depend on the conditions under which the reactions are run.

results are given in Table 5. The calculated values are in good agreement with those obtained experimentally.

Table 5

Amounts of Acid Combined with Wool and Collagen. The Values Given Are in Milliequivalents of Acid per Gram of Protein.

	Calculated Milliequivalents	*Experimental Milliequivalents*
Wool	0.81	0.80[4]
Collagen	0.90	1.0[22]
		0.899[23]
		0.90[26]

The observations of Hitchcock[23] and of Speakman and Stott[23] that deaminated gelatin and wool retain a considerable portion of their acid-combining capacities are of interest, especially since the deaminated materials were prepared under very different conditions. Gelatin was treated for 30 minutes with nitrous acid, and 5.6 mg. of nitrogen, which was equivalent to slightly more than its free amino nitrogen, was removed. Wool was treated for 72 hours and about 9 mg. of nitrogen was removed. This accounts for the free amino nitrogen and nearly 1 atom of nitrogen from the guanidine nucleus. The acid-combining capacities of the deaminated proteins are given in Table 6. The results indicate that the removal of a

Table 6

Acid-Combining Capacities of Deaminated Gelatin and Wool.

	Acid Combined Per Gram Milliequivalents	*Calculated Acid-combining Capacity of the Guanidine Nuclei* Milliequivalents
Gelatin[23]	.44	.56
Wool[3]	.43	.52

nitrogen atom from the guanidine nucleus has not appreciably altered the latter's basic properties. The evidence suggests the possibiltiy that the nitrogen atom which is most readily removed by treatment with nitrous acid is not the nitrogen which combines with the acid.

V. CONCLUSION

The results of the investigation show that when wool, collagen, and arginine are treated with nitrous acid, increasing amounts of nitrogen are evolved with time. The continued evolution of nitrogen is due to the action of nitrous acid on the guanidine nuclei of these materials. Since the evidence indicates that the nitrogen which comes from the guanidine group is not free amino nitrogen, the amino nitrogen contents of wool and collagen are calculated by correcting for the guanidine nitrogen evolved. The values obtained for the percentages of the total nitrogen as amino nitrogen are 2.53 for wool and 2.77 for collagen.

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Proceedings of the American Association of Textile Chemists and Colorists

Bleaching with Chlorine*

By W. L. SAVELL†

ALTHOUGH chlorine has been used for many years as a textile bleaching reagent and, in fact, was the first chemical to be used for the purpose, some of the conditions necessary for the most advantageous preparation and application of chlorine bleaching solutions are not well understood generally.

First, as with a good cocktail, the proper ingredients must be used in correct proportions under suitable conditions and then applied with skill and discretion.

Fortunately the materials required are few and readily available as high quality commercial products. Chlorine in cylinders, multi-unit or single unit tank cars is uniformly high in purity. Liquid chlorine consistently analyzes 99.8% or more which excels in purity the popular brand of soap much advertised as being 99.44% pure. Caustic soda is more variable, its purity depending to some extent on the method of production and subsequent process. A really good grade, suitable for the production of sodium hypochlorite solutions, should have a purity not less than 98.0% and should be particularly low in iron and other metallic impurities.

With these two materials, caustic soda and chlorine alone, bleach liquors may be prepared that will fit the requirements of almost any cotton bleaching problem.

It is common practice to make up a stock solution of bleach liquor which generally contains about 30 grams available chlorine per liter. In some few cases it is prepared at an available chlorine concentration as high as 60 grams per liter. As a matter of good operation, it is well to maintain a standard concentration which will not vary from day to day. This permits the use of regular measured volumes of bleach liquor for given types of goods to be bleached under given conditions.

There is really one variable only, aside from concentration, which should be allowed in a sodium hypochlorite solution to be used for bleaching. The one permissible variable is the excess alkali remaining in the finished solution above the amount required by the direct reaction between the caustic soda and chlorine. In the formation of sodium hypochlorite, 100 pounds of chlorine will react completely with 112.5 pounds of pure caustic soda. If the caustic soda is 99% pure, 113.75 pounds will be required and at a purity of 98% 115 pounds satisfies the reaction with 100 pounds of chlorine. For stability, the solution must be maintained with a slight caustic alkalinity. For this reason, a few pounds of additional caustic soda are added.

The proportion of excess caustic soda which the solution carries has an important influence on the bleaching properties of the finished liquor. If the excess is low, for instance, between .05 and .5 grams of NaOH per liter of stock solution, the bleaching action will be rapid. Light or loose goods easily penetrated, are bleached most satisfactorily with this type of solution at room temperatures. The low alkali content also minimizes the mercerizing action which may be apparent in certain instances if a considerable excess of caustic soda is present in the bleach liquor.

If the texture and preparation of the goods is such as to allow rapid penetration the bleaching action may be speeded by passing the goods through the solution maintained in suitable equipment and then piling in bins. Such exposure to the air permits the carbon dioxide which it contains to react with the slight excess of alkali with the resulting formation of hypochlorous acid. Although the pH will never go below 6.8 under these conditions, the maximum rate of bleaching results.

In bleaching heavier goods or materials not easily penetrated, it is desirable to use a solution that has a lower bleaching rate. In other words, it is preferable to delay the action sufficiently to permit the bleach liquor to penetrate all parts of the goods before the bleaching action starts so that the surface will not be over-bleached and the inner portions under-bleached. Even with this type of goods, however, it is not necessary to have an excess of caustic soda above 1 gram per liter. Any greater excess than this is not only a waste of material, but increases the possibility of partial mercerization and the formation of oxidation products of cellulose with consequent fiber degradation.

There is an idea which has persisted, in spite of proofs to the contrary, that increasing the proportion of excess caustic soda increases the stability of the sodium hypochlorite solution. The truth is, only that amount of caustic soda necessary to protect the surface of the stock solution from the action of carbon dioxide of the air is required for stabilizing purposes. Any further proportion actually decreases the stability slightly and additions

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†The Mathieson Alkali Works, Inc.

beyond the low limit should be dictated by process conditions.

Tests have shown that solutions, made from pure sodium hypochlorite penta-hydrate crystals, are more stable than those of any other composition. Excess alkali in any form decreases the stability.

There is one type of bleaching equipment still in use which calls for a bleach liquor of higher alkalinity than any mentioned previously. The goods are disposed in perforated wooden trays stacked one above another and the bleach liquor circulated by means of a pump to a distributing head above the upper tray. The solution then trickles through the goods from the top tray to the bottom and is then picked up and returned by the pump. Naturally the solution handled in this manner presents a very large surface to the air and the absorption of carbon dioxide rapidly neutralizes the excess caustic soda. If the excess of caustic soda is not sufficient to take care of this condition, the sodium hypochlorite may be converted to hypochlorous acid before the goods have been properly penetrated and the available chlorine dissipated before the bleaching effect has been accomplished. As the time of exposure is a factor in such cases some judgment must be exercised in establishing the proper excess of alkali. In any event, it should not be less than 2.0 grams per liter in the stock solution.

A 30 gram per liter stock solution is generally applied in a dilution of 10 to 12 times the bleach liquor volume or at an available chlorine concentration of 2.5 to 3.0 grams per liter.

Practice varies widely in the application. Goods are immersed in the diluted bleach liquor held at room temperature in concrete tanks and allowed to remain until the color is satisfactory. The time period may be between 1 to 12 hours. In other cases the goods may be padded with the bleach solution and piled in bins as previously mentioned. Circulating kiers are also used in some mills. At least one other mill operates a continuous bleaching system for piece goods in which striped shirtings pass through the solution in 15 minutes. The equipment used is similar to a dye vat. The temperature of the solution is maintained at about 90° Fahrenheit. For this type of operation the temperature of the bleach liquor should not exceed 100° Fahrenheit as conversion of the hypochlorite to sodium chlorate starts about this temperature. At 120° Fahrenheit the conversion is rapid. Sodium chlorate has no bleaching action and reacts detrimentally during the subsequent souring.

Raw stock and waste have been bleached in equipment similar to a pulp beater with the beater roll replaced by a rotating shaft with long curved fingers to circulate the stock. In one case, at least, a temperature as high as 140° Fahrenheit was used for fifteen minutes. Unless very special conditions exist such practice should not be considered.

Still another mill partially bleaches warps on the beam, slightly acidifying the bleach liquor to obtain the effect of hypochlorous acid for brightening.

In the actual preparation of sodium hypochlorite solutions there are several points of first importance that should be observed. The equipment used for the makeup and handling of solutions should be constructed of materials which are inert to the solution. Iron, brass, bronze, nickel, copper and their ordinary alloys are immediately eliminated. Any contact with these metals will catalyze the decomposition of a sodium hypochlorite solution and destroy its stability. Tanks may be made of concrete, vitrified tile, stoneware or rubber lined steel. Pipe lines, valves, fittings and pumps for handling these solutions are best rubber lined or made of hard rubber. The latter material is rather fragile and should be protected with suitable guards in exposed places. Tile or stoneware pipe and fittings are used in some installations with entire satisfaction. The importance of avoiding possible contact of the sodium hypochlorite solution with ordinary metals cannot be over-emphasized.

The pipe line from the chlorine container to the top of the solution tank may be made of copper, brass or iron. Generally, a flexible copper tube is used to connect the container to the chlorine pipe line. Iron pipe is most commonly used to carry the chlorine to the top of the makeup tank. From this point extra heavy chemical lead pipe or a silver tube conducts the chlorine to the bottom, with the end of the tube directed toward the center of the tank.

In some instances the only valve in the line is the one on the chlorine container although it is preferable to have a valve and a vacuum break at the top of the makeup tank for control purposes. At this point it is well to stress another precaution necessary to prevent contamination of the liquor with metallic impurities.

When the control valve is closed and the flow of chlorine stopped there remains in the line between the valve and the end of the delivery line a certain amount of chlorine which slowly dissolves in the liquor. In the course of a relatively short period of time the solution rises in the pipe until it is in direct contact with the control valve. As a result the valve is rapidly corroded and the next batch of liquor is contaminated with the metallic impurities when the valve is again opened for chlorination. Subjected to such conditions the control valve must be replaced often.

To avoid the possibility just described, a vacuum break designed for chlorine must be installed in the line beyond

Fig. 1—The Mathieson Automatic Vacuum Break is sturdily constructed for years of trouble-free service.

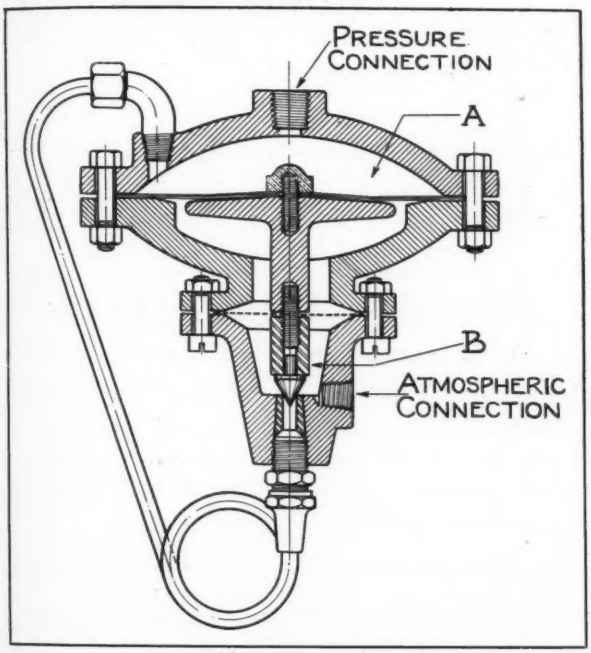

Fig. 2—Internal construction of the vacuum break, showing position of the diaphragm and valve assembly.

(on the outlet side) the control valve. See Figs. 1, 2 and 3. This device admits air to the line as the absorption of the chlorine tends to establish a vacuum and prevents the solution from rising to the control valve. As soon as the chlorine pressure is re-established by opening the control valve the vacuum break closes automatically.

Anyone who has made up a solution of sodium hypochlorite with caustic soda and chlorine knows that the reaction develops a noticeable amount of heat. If liquid chlorine is used the heat evolved will raise the temperature of the solution approximately .6° Fahrenheit for each

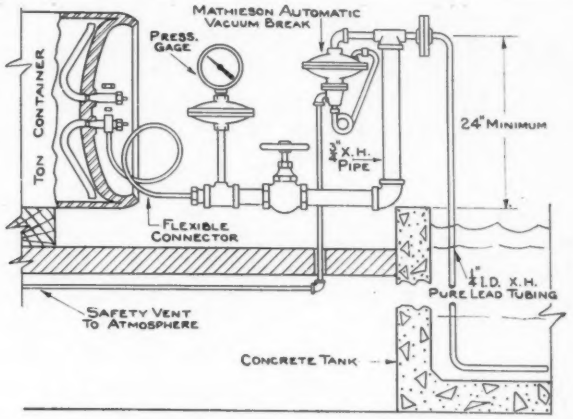

Fig. 3—Standard method of connecting the vacuum break in the line when the chlorine container is above the level of the liquid being chlorinated.

gram per liter absorbed. That means a stock solution made up to 30 grams available chlorine per liter will show a total increase in temperature of 18° Fahrenheit. If chlorine gas is used the temperature increase becomes .7° Fahrenheit for each gram per liter or a total temperature increase of 21° Fahrenheit in making up a solution of 30 grams per liter concentration.

The figures will vary somewhat in practice depending upon the heat capacity of the tank and the relative volume. In any event, they will approximate those given, possibly being slightly lower.

There is an importance in the temperature condition of the solution which is often overlooked. Knowing that the temperature increase is 18° Fahrenheit in producing the usual stock solution, it is necessary to relate it to the optimum finishing temperature. This is at 100° Fahrenheit although much lower temperatures have been advocated in the past. Finishing at 100° Fahrenheit insures the greatest possible stability, and after settling, a clear greenish yellow solution. The effect of the relatively high temperature is to precipitate any small amount of im-

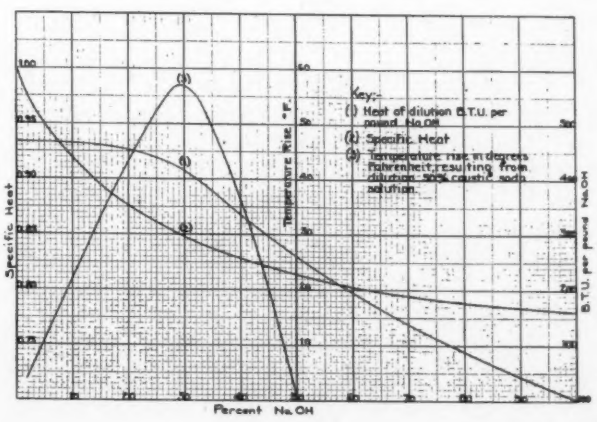
Specific Heat
Temperature Rise °F.
B.T.U. per pound NaOH
Percent NaOH
Key:-
(1) Heat of dilution B.T.U. per pound NaOH
(2) Specific Heat
(3) Temperature rise in degrees Fahrenheit, resulting from dilution 30% caustic soda solution

Fig. 4.

purities which may have been present in the caustic soda or picked up from equipment. By this means even the smallest traces of iron are eliminated.

In order to finish the solution at the desired temperature the chlorination should be started with the caustic soda solution at approximately 82° Fahrenheit. This consideration fits well into operating conditions as it shortens the time required for cooling the caustic soda solution prior to chlorinating. Temperature increases and heats involved in preparing solutions from solid caustic soda and 50% liquid caustic are shown in the curves on the attached chart (Fig. 4).

The following tables show quantities required for producing stock solutions with various caustic soda residuals:

Stock Solution of Sodium Hypochlorite
30 Grams Available Chlorine Per Liter

Wt. of Chlorine Pounds	*Wt. of Caustic Soda—Pounds* 100%	99%	98%	95%	*Volume of Caustic Solution Gallons*	*Residual NaOH Grams Per Liter*
100	112.50	113.75	115.0	118.5	394	0.0
100	112.67	113.83	115.2	118.7	394	0.05
100	112.84	114.20	115.4	119.0	394	0.10
100	113.18	114.40	115.4	119.2	394	0.20
100	113.52	114.80	115.9	119.5	394	0.30
100	113.86	115.20	116.3	119.8	394	0.40
100	114.20	115.50	116.6	120.4	394	0.50
100	117.54	118.80	120.0	123.7	394	1.00
100	120.88	122.10	123.2	127.2	394	2.00

If 150 pounds of chlorine is the unit the caustic soda weights given in this table should be multiplied by 1.5. The volume of caustic soda solution should also be increased by this amount. For a one-ton unit of chlorine the caustic figures should be multiplied by 20.

Where stock solutions of higher strength are desired, the volume of caustic soda solution should be decreased, as shown in the following table:

For 100 Pounds of Chlorine Used as Liquid

Av. Cl. Grams Per Liter	*Vol. of Caustic Gallons*	*Total temp. increase Degrees Fahrenheit*	*Temp. of Caustic Sol. Before Chlorination Degrees Fahrenheit*	*Finishing Temperature Degrees Fahrenheit*
30	394	18.0	82.0	100.
40	300	24.0	76.0	100.
50	232	30.0	70.0	100.
60	185	36.0	64.0	100.

As previously indicated, the temperature of the caustic soda solution before starting chlorination may have to be varied somewhat to compensate for the heat capacities and radiation properties of the makeup tank.

It is always desirable to use liquid chlorine direct as its use eliminates the installation of a chlorine evaporator or necessity for connecting a large number of containers to the line. The chlorinating time is also shortened to a maximum period of one hour.

In this article the composition of the usual organic impurities associated with cotton fiber has not been discussed. It should be mentioned, however, that good bleaching depends on satisfactory preparation of the goods before they reach the bleaching process. Under the pressure of a large volume of business which may tax the capacity of the boil-off equipment this latter process may be slighted and the bleaching treatment depended upon to make up for the deficiency. When this is done it is usually at the sacrifice of quality in the finished goods. Every effort should be made to bring the goods to the bleaching operation as free as possible from oils, fats, waxes, pectins or other impurities. This also refers to iron stains. No oxidizing bleach can be expected to remove stains of metallic origin.

As a brief summary of desirable conditions for cotton bleaching, it may be said that the smallest amount of bleach solution should be used which is satisfactory for the purpose. A standard strength of stock solution well maintained will assist materially in determining the correct amount. The lowest workable alkalinity should be established in the stock solution as increasing alkalinity favors the degradation of fiber. This is particularly true in heated bleach solutions. The active bleaching period should be kept at a minimum for the degree of bleaching desired.

Analytical Methods for a Textile Laboratory

The Council of the A.A.T.C.C., believing that Dr. Scott's series of articles entitled "Analytical Methods for a Textile Laboratory" might well be brought together in book form, have proceeded with its publication. Copies may be obtained from the Secretary of the Association, Harold C. Chapin, Lowell Textile Institute, Lowell, Mass., for 75 cents.

STANDARD SILK SAMPLES

There have been prepared, under the direction of the Sub-Committee on Fastness of Dyed Silk, standard dyed silk fabrics to represent four classes of fastness to washing—namely, Class I, Class II, Class III and Class IV. These standards have been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1931 Year Book.

The A.A.T.C.C. is prepared to furnish sets of these washing standards for a nominal charge which will cover the cost of preparation. It will be possible to accurately grade the fastness by comparing it with the standards after subjection to the standard washing tests approved by this Association. All inquiries concerning these Silk Washing Standards may be addressed to the Chairman of the Research Committee.

Louis A. Olney,
Lowell Textile Institute,
Lowell, Massachusetts

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—H. C. Chapin, Secretary, Lowell Textile Institute, Lowell, Mass.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

Note. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the American Dyestuff Reporter.

A-3

Education—Ph.B., Brown University, 1920. Two years post-graduate work at M.I.T.

Experience—2 years instructor at M.I.T. 2 years as research chemist in print works (Gum thickenings, application of dyes, dye testing and evaluation. 4 years as chief chemist in bleaching, mercerizing, dyeing and finishing plant. 4½ years as research and plant chemist in silk mills (Colorimetric work in color matching, dye testing and identification and testing of chemicals). 2 years as organic research chemist (laboratory and semi-plant research on organic chemicals, intermediates and dyestuffs). Age 35, married. Will go anywhere, references.

A-5

Education—B.T.C., Lowell Textile Institute.

Experience—Assistant chemist in carpet mill, dye tester in dye plant, research and analytical work in silk dyeing and finishing plant laboratory, plant chemist and overseer of bleaching in surgical dressing plant, assistant chemist in woolen mill. Age 29. Married.

A-6

Education—Analytical Chemistry and Dyeing Course, Lowell Textile Evening School.

Experience—Seven years as print color and dye chemist in printing, dyeing and finishing plants; recently in charge of textile printing department of dyestuff manufacturer.

A-8

Education—B.T.C., Lowell Textile Institute.

Experience—Assistant chemist in carpet mill, five years; dye testing, analytical and general mill control work. Age 29, married.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-4

Education—B.T.C. 1934, Lowell Textile Institute.

Experience—Assistant chemist in cotton knitting plant; second-hand in woolen knit goods dye house. Will go anywhere; references.

A-B-5

Education—Graduate of the University of Lausanne, Switzerland. Doctor's degree in Chemistry. Knowledge of French and German.

Experience—Eleven years with large bleaching, dyeing, printing and finishing plant as assistant Chemist and then Chemist in charge of the Laboratory. Experience in dyeing and printing cotton and rayon fabrics; research and analytical work.

A-B-C-1

Education—Graduate Industrial Chemical Engineer, Pratt Institute—1911.

Experience—One year as plant control chemist, 4 years as laboratory chemist with gas company, 13 years as plant chemist with bleaching, dyeing and finishing plant. (Rayon and cotton piece goods). Formulated processes and put them into plant operation, 1 year as chemist and demonstrator for dyestuff company, 1 year as superintendent colorist with print works printing linen and rayon, 1 year as director of testing laboratory for national dry goods concern.

A-B-C-2

Education—Graduate of Lewis Institute of Engineering of Chicago and graduate of Philadelphia Textile School (Chemistry and Dyeing department).

Experience—Has had extensive experience as assistant chemist and colorist in silk printing, dyeing and finishing; also dyeing raw stock wool; and dyeing and finishing cotton and rayon. Age 30; married; references.

A-B-C-3

Education—3 years at Brown University and Drexel Institute.

Experience—2½ years in dyestuff laboratory; 3 years as second-hand, dyeing indanthrene and direct colors on rayon skeins; 6 months as boss dyer on silk and cotton ribbons and hosiery; 3 years overseer of dyeing and finishing rayon tubing. Can handle laboratory, dyehouse, finishing or outside service. Age 30; married.

A-C-1

Education—4 years at Newark Evening Technical School in Chemical Engineering.

Experience—8 years in manufacturing, research, testing of soaps, oils, gums and finishes and application of same in all phases of the textile industry. Age 23, single. References.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton lacks, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—Eight years as boss dyer on skeins and ribbons. Over ten years as chemist and head dyer for a large hosiery mill. Experienced on Silk, cotton, rayon and wool in skeins, ribbons, piece goods and all kinds of mixtures. Willing to go anywhere. Not afraid to work or face responsibility. Can handle help efficiently.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies' and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-9

Experience—Hosiery dyer with fifteen years' experience on high grade silk hosiery; familiar with all types of machines. Age 43, married. Will go anywhere.

B-12

Education—2 years days at N. Y. U. and 3 years nights studying chemical engineering.

Experience—1½ years asst. colorist, 5½ years colorist. Experienced on vats, commercial and fast colors on cotton and cotton-rayon mixtures. References; age 29; married.

B-13

Experience—Large experience as an assistant colorist chemist in silk printing, dyeing and finishing; also on cotton and wool dyeing. References.

B-14

Education—Rhode Island School of Design.

Experience—Familiar with all classes of wool dyeing. Seven years with large carpet mill as dyer and processor of washed oriental rugs. Will go anywhere, married, 37 years old. References.

B-15

Education—B.T.C., Lowell Textile Institute, 1934.

Experience—Experience in dye house running washers, dye kettles and as a dye weighter.

B-16

Education—Chemistry and Dyeing Dept., Philadelphia Textile School.

Experience—Head dyer and chemist on all types of hosiery; dyeing silk, cotton, Bemberg, rayon and unions of same; Celanese and immunized cotton effects. Age 27, married. Will go anywhere.

B-17

Education—Lowell Textile Institute (Chemistry and Dyeing Course) 1916; extension courses at Brown University.

Experience—6 months dyeing wool at finishing company; 2½ years research work on bleaching, dyeing and finishing at dye works; inspector of textile equipment, U. S. Ordnance Dept., during war; 15 years as superintendent of dyeing at finishing company, including all types of colors on cotton piece goods and some rayon and celanese; handled chemical work at last named plant for many years as well as dyeing. Age 40, married, prefers East. References

AMERICAN
DYESTUFF
REPORTER

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Vol. XXIV April 8, 1935 No. 7

THE TEXTILE PROCESSING SHOW

IN our issue of March 25th we published several letters which we had received in response to our editorial concerning a textile processing show which appeared in our issue of February 11th. We feel called upon to comment on certain of these letters, not with the idea of criticizing unfavorably the ideas of the writers, but rather to further enlarge our viewpoint upon the matter.

In one letter it was stated that the A. A. T. C. C. could not sponsor or cooperate in the promotion of such a show without involving itself in the endorsement of articles exhibited or otherwise becoming entangled with the sales promotion of certain products. We, ourselves, cannot share this viewpoint. To our knowledge exhibitors in other textile shows have not, in any way, utilized the fact that they have exhibited to indicate that their product has received the endorsement of the sponsors of the show. In the case of the proposed show if there is any danger of such action an agreement between the Association and exhibitors can forestall it. However, we doubt very much whether this will be necessary as we do not see how any exhibitor can presume to advertise that his product has received the endorsement of the Association unless he has received from the Association a written statement to that effect. This, of course, the Association can refuse to do.

Another letter brings forth the proposal that any profits resulting from such a show should be divided among the exhibitors and further states that there is no reason why the Association should receive any compensation for the privilege of exhibiting inasmuch as the show would make the meetings more attractive and would result in greater attendance. We do not agree with the latter part of this statement because the meeting and the show would tend to increase the attendance at both over what it would be if either were to be held at separate times. We think that the Association should be entitled to a portion of the profits to further its research program. We believe, however, that the thought advanced in the first portion of the paragraph warrants further attention. A division of profits among the exhibitors would bring down the cost of the display for each concern involved. This would be a distinct advantage to the exhibitors inasmuch as there is considerable expense involved in the preparation of an attractive display especially where the machinery manufacturers are concerned.

In this connection we have another idea to advance,—one that we think should meet with favor among prospective exhibitors and the members of the Association. We would suggest that an association of exhibitors be formed to carry out further plans for the promotion of the proposed show and to make arrangements for the cost of the exhibition to be pro-rated among the exhibitors—making allowances for a certain percentage of the receipts to be turned over to the A.A.T.C.C. This plan would relieve the A.A.T.C.C. of any commercial connection with the show and therefore would answer any objections raised on that account. Essentially the A.A.T.C.C. is a research organization and we do not propose to suggest anything that would harm its position in this regard but we cannot see that a textile processing show, which should be of interest to the members of the Association, held at the time of the Annual Meeting would detract in any manner from the prestige of the Association.

Still another letter holds that the proposed show would duplicate, more or less, the present shows held at Greenville and Philadelphia. We do not mean to detract from these shows but it seems logical that some of the exhibitors now displaying their products at these shows could more profitably take space at a textile processing show. The two shows mentioned are what might be termed "manufacturers' shows" and appeal more to the manufacturer of textile materials. We think the manufacturers of wet processing machinery, chemicals and dyestuffs would do well to concentrate their efforts upon the people who buy and use their products,—the dyers, finishers and chemists.

If you have not written to us stating your opinion of the suggested exhibition please do so, in order that we can form as accurate a picture as possible concerning the thoughts of all concerned. There follow abstracts of further letters which we have received; we are not publishing them in their entirety as they more or less duplicate the subject matter contained in the letters already published.

COMMUNICATIONS RE PROCESSING SHOW

The idea of a textile processing show, if confined to wet processing as outlined in your recent editorial, seems of value. There is a doubt in my mind as to how interested the men in the woolen mills of the North would be in a Chattanooga show. Perhaps another year the woolen end could be brought to the front in a northern city.

RAYMOND STEVENS,
Chief Chemist, The Felters Co.

We feel that the expense which would be involved would not be worth while and we would much prefer to depend on the individual contacts of our salesmen during their routine calls on the trade.

H. R. TISDALE,
American Dyewood Co.

Excellent idea, providing ballyhoo is kept out. Should prove exceedingly valuable to the textile industry in general and textile chemists and colorists in particular.

EPHRAIM FREEDMAN,
Chairmn, N. Y. Section, A.A.T.C.C.

The editorial is timely and brings out splendidly the need of such an exhibition. Moreover the idea of a "traveling exhibition" possesses many advantageous points and would serve many-fold purposes of coordinating the many divisions of the textile wet-processing industry and bringing it to the attention of the interested parties in the textile industry.

CHARLES B. ORDWAY,
Assoc. Prof., Tex. Chemistry and Dyeing,
Alabama Polytechnic Inst.

The idea seems good but as we already have one show in Philadelphia each year I doubt very much if an additional show would interest us. Possibly by starting in a small way, just a couple of days during the annual meeting, might be worth while.

A. B. MCCARTY,
American Aniline & Extract Co.

• COMMUNICATION RE TEXTILE CHEMICALS

The following letter is self-explanatory and we would suggest that manufacturers of chemicals used in the textile field communicate directly with Dr. Chwala whose address is given in the letter.

Editor,
AMERICAN DYESTUFF REPORTER,
Dear Sir:

Dr. A. Chwala, whose address is Linzerstrasse 454, Wein, XIII/5, Austria, informs me that he is preparing a book entitled "Colloids and Colloidal Electrolytes in the Textile Industry," and in order that full credit and information about American products and processes may be included, he asks that American manufacturers of these products mail him their circulars, pamphlets, prospectuses, etc., dealing with the various products of this character that they manufacture. Dr. Chwala is also to give an address before the International Association of Chemists and Colorists on "The Colloid Nature of Textile Assistants," such as sizing and de-sizing materials, thickeners, softeners, emulsions, dispersers, wetting-out agents, detergents, delusterers, dye assistants, etc., etc., and desires to give due credit to all who can furnish him with data as to reliable products and processes, both for his book and his lecture.

Through your journal, the AMERICAN DYESTUFF REPORTER, I trust that you will request all those interested to mail to Dr. Chwala such publications and information as they feel are pertinent and desirable. He is Privatdozent at the technischen Hochschule in Vienna.

Sincerely,
JEROME ALEXANDER

ALFRED L. LUSTIG

Alfred L. Lustig, president and general manager of the Apponaug Company, died recently in Florida, where he had been spending the winter months.

Mr. Lustig was well known in the textile field, being distinguished as one of the leading textile chemists and colorists in this country. He was born in Hungary in 1865, graduated from the Vienna School of Technology at the age of 20, and, after coming to this country, entered the employ, in 1888, of Heller & Mertz, manufacturers of color and pigment. He left this company to go with the Cranston Print Works, where he spent a year, and then returned to Heller & Mertz. He again left this company, and, after spending some time as assistant superintendent and chemist of the Merrimac Manufacturing Company, he again became associated with the Cranston Print Works, in 1897. In 1899 he became superintendent of the Glenlyon Print Works. Fourteen years later he organized the Acme Finishing Company, and became its first general manager. In 1913 he was made general manager of the Apponaug Company, which position he retained until his death. He became president of this organization upon the death of J. P. Farnsworth.

Mr. Lustig was active in several associations connected in his field of work, including the A. A. T. C. C., the A. C. S., the Colorists' Club, and the Society of Dyers and Colourists in England. He was also a director of the Providence Dye, Bleach and Calender Company, and a vice-president and director of the U. S. Institute for Textile Research.

The deceased is survived by his wife, three sisters who live in Hungary, four daughters and eight grandchildren.

NEW PATENTS

(*Abstracted by S. O. C. M. A.*)

Oil-Soluble Azo Dye. (Otainable by coupling betanaphthol with an aminoazoxylene; suitable for coloring gasoline.) Ralph B. Payne, Elmira, N. Y., assignor to National Aniline & Chemical Co., Inc., N. Y., N. Y., No. 1,986,116, Jan. 1, 1935.

Dye Producing Composition. (Comprises mixing the condensation product of ortho-amino-diphenyl-ether and piperidine carboxylic acid with beta-hydroxy naphthoic acid -4-chlor-2-amino-anisidid; valuable as dyes in substance as well as in dyeing and printing processes, when printed yield clear scarlet shades on cotton and rayon, fast to light, rubbing, kier boiling and chloring; yellow and blue shades also obtainable.) Eugene A. Markush, Jersey City, N. J., assignor to Pharma Chemical Corp., New York, N. Y., No. 1,986,276, Jan. 1, 1935.

New Cellulose Derivatives and Their Manufacture. (Comprises acting with an aqueous solution of an amine on hydroxy groups directly attached to cellulose residues until the product contains fixed nitrogen; possess an affinity for acid dyestuffs. A continuation in part of U. S. application Serial No. 492,363, filed Oct. 30, 1930, corresponding to British application No. 36,474/29.) Henry Dreyfus, London, Eng., No. 1,986,881, Jan. 8, 1935.

2-Alkylaminobenzene - 1 - Carboxylic Acid - 4 - Sulfonic Acids. (Valuable intermediates for dyestuffs and synthetic drugs, prepared by causing a suitable primary aliphatic amine, such an propylamine, butylamine, isobutylamine and the like, to act upon a 2-halogenbenzene-1-carboxylic acid-4-sulfonic acid or an alkali metal salt thereof in aqueous solution and at elevated temperature; a division of Patent No. 1,960,644, May 29, 1934.) Anton Ossenbeck, Cologne-Mulheim, and Ernst Tietze, Cologne-on-the-Rhine, Ger., assignors to General Aniline Works, Inc., New York, N. Y., No. 1,987,266, Jan. 8, 1935.

Water-Soluble Anthraquinone Dyestuffs and Process for Making Same. (More specifically, comprises heating a 1-amino-2-sulfo-4-halogenanthraquinone with a 4-amino-1-methyl-benzene-2-sulf-(alkyl) amide in presence of acid binding agents; dye animal fibers blue shades of excellent fastness to milling, washing, perspiration and light.) Albin Peter, Basel, Switzerland, assignor to firm "Chemical Works, formerly Sandoz," Basel, Switzerland, No. 1,987,538, Jan. 8, 1935.

Sulfur Dyestuff Preparation. (For cotton printing, comprising Indocarbon CL, glycerine and an alkali metal salt of tetrahydronaphthalene-beta-sulfonic acid.) Herman Berthold, Leverkusen-I.G. Werk-on-the-Rhine, Ger., assignor to General Aniline Works, Inc., N. Y., N. Y., No. 1,987,583, Jan. 8, 1935.

Dyestuffs of the Anthraquinone Series. (More specifically, comprises sulfonating 1-amino-2-acetyl-4-bromanthraquinone in sulfuric acid monohydrate, then treating the sodium salt with potassium acetate, para-toluidine and cuprous chloride; dye wool blue to green shades.) Paul Nawiasky and Otto Grosskinsky, Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Works, Inc., N. Y., N. Y., No. 1,987,747, Jan. 15, 1935.

Vat Dyestuffs of the Dibenzopyrene-Quinone Series. (More specifically, comprises acting on 3,4,8,9-dibenzopyrene-5,10-quinone with bromine in chlorosulfonic acid in the presence of iodine; give bright clear yellow to orange dyeings of excellent fastness to light and to boiling, possessing a very good affinity to vegetable fiber.) Max Albert Kunz, Mannheim, Georg Kranzlein, Frankfort-Hochst-on-the-Main, Karl Koeberle, Ludwigshafen-on-the-Rhine, Martin Corell, Frankfort-Hochst-on-the-Main, Erich Berthold, Ludwigshafen-on-the-Rhine, and Heinrich Vollmann, Frankfort-Hochst-on-the-Main, Ger., assignors to General Aniline Works, Inc., N. Y., N. Y., No. 1,988,205, Jan. 15, 1935.

Nitrogenous Polymerization Product. (Of benzo nitrile, partly dyestuffs and partly valuable intermediate products for dyestuffs, and also for pharmaceutical purposes, vulcanization accelerators and the like.) Max Albert Kunz, Mannheim, and Karl Koeberle and Erich Berthold, Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Works, Inc., N. Y., N. Y., No. 1,989,042, Jan. 22, 1935.

Vat Dyestuffs of the Acridone and Thioxanthrone Series and the Process of Making Them. (Dye cotton violet-yellow-brown-orange shades.) Paul Nawiasky, Ludwigshafen-on-the-Rhine, Wilhelm Bauer, Leverkusen, and Emil Krauch, Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Works, Inc., N. Y., N. Y., Reissue 19,437, Jan. 22, 1935.

Amine of High Molecular Weight. (More specifically, the cocoanut oil fatty acid derivatives, being generally valuable auxiliary products, especially in the textile industry.) Wilhelm Lommel, Leverkusen-Wiesdorf, and Rudolf Schroter, Leverkusen, Ger., assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Ger., No. 1989,325, Jan. 29, 1935.

Azo Dyestuff. (A new fast direct black for cotton.) Heinrich Clingestein, Cologne-on-the-Rhine, and Myrtil Kahn, Cologne-Riehl, Ger., assignors to General Aniline Wks., Inc., N. Y., N. Y., No. 1,989,472, Jan. 29, 1935.

Vat Dyestuffs of the 1.2-Benzanthroquinone Series. (Substantially dichlordibenzoyleneanthanthrene, dyeing cotton reddish blue shades.) Heinrich Neresheimer, Ludwigshafen-on-the-Rhine, Willy Eichholz, Mannheim, and Georg Boehner, Edingen-on-the-Neckar, Ger., assignors to General Aniline Wks., Inc., N. Y., N. Y., No. 1,989,493, Jan. 29, 1935.

Chromiferous Azo-Dyestuff and Process of Making Same. (Dyeing wool blue tints of very good fastness, particularly to rubbing, and excellent color in the artificial light.) Fritz Straub, Basel, and Hermann Schneider, Riehen, near Basel, Switzerland, assignors to Society of Chemical Industry in Basle, Basel, Switzerland, No. 1,989,567, Jan. 29, 1935.

Chromiferous Dyestuffs and Process of Making Same. (From an ortho-hydroxy-amino-naphthalene sulfonic acid which contains no nitro-group and a 2-hydroxynaphthalene, dyeing wool navy blue tints of very good fastness properties and excellent appearance in the artificial light.) Fritz Straub, Basel, and Hermann Schneider, Riehen, near Basel, Switzerland, assignors to the firm of Society of Chemical Industry in Basle, Basel, Switzerland, No. 1,989,568, Jan. 29, 1935.

Chromiferous Dyestuff and Process of Making Same. (Dyeing wool blue, navy-blue and blue-black tints of very good fastness properties and excellent appearance in the artificial light.) Fritz Straub, Basel, and Hermann Schneider, Riehen, near Basel, Switzerland, assignors to the firm of Society of Chemical Industry in Basle, Basel, Switzerland, No. 1,989,569, Jan. 29, 1935.

Chromiferous Dyestuff and Process of Making Same. (For example, the azo-dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene treated with potassium chromite; dyeing wool blue to navy blue tints of very good fastness properties and excellent appearance in the artificial light.) Fritz Straub, Basel, and Hermann Schneider, Riehen, near Basel, Switzerland, assignors to Society of Chemical Industry in Basle, Basel, Switzerland, No. 1,989,570, Jan. 20, 1935.

Anthraquinone-Acridone Imide Compounds and Their Production. (New anthracene dyestuffs and intermediates; more specifically, comprises condensing an anthraquinone-benzacridone-carboxylic acid chloride with an amino-anthraquinone in an inert organic solvent, producing fast orange shades.) Alexander J. Wuertz, Wilmington, Del., assignor to E. I. du Pont de Nemours & Co., Wilmington, Del., No. 1,989,904, Feb. 5, 1935.

Hydroxy Fluoranthenes. (For instance, 8-hydroxyfluoranthene-9-carboxylic acid, a dyestuff intermediate.) Alfred Bergdolt, Cologne-on-the-Rhine, and Fritz Ballauf, Cologne-Mulheim, Ger., assignors to General Aniline Wks., Inc., N. Y., N. Y., No. 1,990,010, Feb. 5, 1935.

● MARCH TEXTILE RESEARCH

The March number of *Textile Research,* official publication of U. S. Institute for Textile Research, Inc., contains the conclusion of the Textile Foundation study by M. S. Campbell of "The Disposal and Recovery of Textile Waste Liquors," and the following research reports of special interest to silk manufacturers: "Diameter Ratio of Silk Filaments as Related to Two-Tone Dyeing" and "The Deterioration of Silks by Light of Different Wave-Lengths."

Mr. Campbell gives a detailed description of a chemical precipitation treatment of the waste liquors from the process of printing cottons which, followed by rapid sand filtration, produces an effluent suitable for discharge into streams containing fish and plant life, or for discharge into sewage treatment plants. Mr. Campbell's study was conducted with an experimental plant at the Proximity Print Works, Greensboro, N. C.

One of the most insidious and troublesome causes of two-tone dyeing in silk fabrics has been traced by Fred Mennerich, chemical engineer, Holeproof Hosiery Co., Milwaukee, Wisc., and O. A. Hougen, director of laboratories, U. S. Testing Co., Inc., to a difference in the average diameter ratios of silk filaments in two adjoining sections of the same fabric. The discovery proves that it is futile to attempt to correct for this particular cause of two-tone by chemical adjustments in soaking, boiling-off or dyeing. It emphasizes again the danger of mixing lots of cocoons at the filatures.

A study of the deterioration of silks by light of different wave-lengths, conducted by Esther Bruner and Mina Goehring, Department of Home Economics, Kansas Agricultural Experiment Station, Manhattan, Kan., developed the following results: Lead-weighted silk showed greater deterioration upon exposure to regions of the spectrum studied than did pure-dye or tin-weighted silks. The greatest deterioration in all of the silks under observation occurred during exposure to the entire region of the spectrum. Decrease in tensile strength under exposure to an unfiltered light source is due primarily to those rays below 3,490 angstrom units. Deterioration appears to become more rapid as the time of exposure is increased beyond 72 hours, particularly in the case of lead-weighted silks.

TECHNICAL NOTES

Continued from page 178)

dermatitis caused by wearing of furs dyed with p-phenylene-diamine has its origin in traces of the diamine which have escaped oxidation, and slowly oxidize in the air after some time. The dyestuffs formed by complete oxidation certainly have no effect upon the skin; but the dyeings (distinguished from the completely formed dyestuffs) are a very frequent cause of dermatitis. Blumenthal and Jaffe cite records to the effect that in England, during two winter months in 1922, about one thousand cases of Ursol eczema were observed. Cox states, that, in an Edinborough hospital, during eleven years, 2,527 cases of dermatitis were treated, but of this number only 157, or 6%, could be traced to the wearing of furs.

Blumenthal and Jaffe also give definite figures for other amines and diamines; e.g., out of 86 cases under their observation, or the records of which they studied, 26 were ascribed to aniline, 24 to amino-azo-toluene, 21 to p-phenylene-diamine, and 15 to p-aminophenol.

Picric acid and Martius' Yellow have long been known as skin irritants; Koelsch remarks this also. Georgevics gives Aurantia (hexanitro-diphenylamine) the same evil reputation.

All of the above has dealt with purely organic substances. Cox cites dyestuffs containing appreciable amounts of As, Sb, Ag, Cu, Cr, Ni, and possibly Pb, as also under suspicion. It may be that the irritant properties of such triphenyl-methane dyestuffs as Malachite and Brilliant Greens may be due to their considerable content of zinc chloride. Dyestuffs applied with mordants also often cause trouble, when the dyestuffs themselves have a clean record. Even protectives against moths, such as naphthalene, p-dichlorbenzene, and ethereal oils, are known to produce eczema upon some skins.

The subject at present is in a perplexed condition, certainly.

Bleaching and Dyeing of Feathers

By **OLGA HOTCHKINSEY**

FEATHERS consist of two main parts, the horny quill and butt, and the flues, or soft "feathery" portion. Some feathers are soft and supple, such as for instance, ostrich and paradise bird plumes; others are hard, like those from the wings and tails of the domestic fowl, duck and goose. Feathers for use in filling cushions, upholstery of automobiles, bed-ticking, etc., are seldom dyed. Such stock, if of best quality, is sometimes bleached with peroxide of hydrogen or bisulfite of soda after scouring. Cheaper qualities containing a percentage of colored feathers are scoured only.

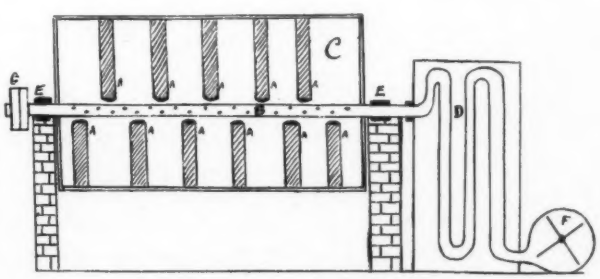
The usual detergents employed in cleansing feathers comprise soap and ammonia, or soap and pearl-ash. Soap and soda ash are not often used for scouring the best white feathers for bleaching as the combination is alleged to induce yellowing of the flues. Nevertheless, these detergents are sometimes used in scouring colored feathers which are in a very dirty condition. If the feathers are somewhat bloodstained, they are soaked in a warm bath containing sufficient ammonia to soften the blood-clots. After this has been done, the stock is scoured with soap and pearl-ash in the usual manner.

The fluffy kind of feathers such as are used for stuffing cushions and upholstering etc. are best scoured in coarse hessian bags for the sake of easy handling during processing. About 2 lbs. of feathers should be filled into each bag; crowding of the contents should be avoided or the feathers will not be properly cleansed, since free circulation of the scouring liquor will be hindered. Scouring of bulk lots of loose feathers in open tubes is seldom done, owing to the considerable amount of time required in wetting out the stock, especially in the instances of duck and goose plumage, since these feathers contain a good deal of water-repelling oil. On the other hand, if the feathers are packed in bags, it is a simple matter to thrust each bag under the surface of the scouring liquor with a pole, and to retain it there until the contents have become saturated.

After immersion of the stock, the bags are well pounded in the warm scouring liquor by means of a pole. The material is then left to steep for fifteen minutes, then rinsed in clean warm water until free from suds. If the stock is to be bleached, the bags are plunged into the bath of bleaching liquor and allowed to remain therein until the feathers are satisfactorily decolorized. For the peroxide bleach, the bath is prepared with 1 pint hydrogen peroxide 12 vols., per 10 lbs. of feathers. After the bath has been made feebly alkaline with ammonia, the stock is entered and well pounded for a few minutes. The bath is then heated during half an hour to about 120° F., after which steam is turned off and the feathers left to steep in the cooling bath for 8 or 10 hours. The bags are then lifted and after draining, they are plunged into a rinsing bath containing cold water.

If the feathers are to be bleached with bisulfite of soda the bath is set with 1½ pints of bisulfite of soda 70-80° Tw. and 1 fluid ounce of sulfuric acid per 10 lbs. of feathers. The stock is allowed to steep in the cold, freshly prepared bleaching bath for one or two hours, after which it is rinsed in clean cold water. The bisulfite bleach is a cheaper process to carry out than the peroxide bleach but the white is not so lasting as in the other instance, the feathers gradually assuming a yellowish hue.

After the feathers have been bleached, they are hydro-extracted, then emptied out of the bags into a chute. They are blown along this by a draught of air from a rotary blower, and then are deposited in a large cyclinder covered with fine-mesh rustless wire netting, and fitted with a series of internal baffles in order to agitate the stock.



When this contrivance has been filled with feathers, it is set into motion and during the slow rotations upon the central shaft, the feathers are dried by exposure to the current of hot air forced through a series of small holes bored in the cylinder shaft. (See illustration.)

It is rarely that upholstery feathers require coloring after scouring, for most consumers prefer undyed material. Where dyeing is necessary, processing is done with acid or basic colors, the assistants used being acetic or oxalic acids, since the presence of residual sulfuric acid in the feathers depreciates the resiliency of the material, hence cushions filled with such stock show poor recovery to crushing. The most suitable acid colors to use for coloring feathers are those with good affinity for the material when applied below the boil; since to boil the bath for any considerable time, depreciates the lofty character of the feathers.

The following acid dyes are suitable:— Patent Blue A types; Croceine Scarlet; Roccelline; Indian Yellow; Sulfoncyanine Navy and Black; Acid Violet S4B type; Fast Acid Violet AZR type; Orange II; Acid Green. In order to cause the dyestuff to penetrate the butts and stem of the feathers, they must be entered into the dyebath at or near boiling point, since the use of this tmeperature softens the horny substance composing the butt or stem. Dyeing is then continued in the cooling bath. The stock may either be processed in bags or in a wire mesh cylinder which is made to rotate slowly in the dyebath.

● NEW NATIONAL DYES

National Aniline & Chemical Co. announces release of the following new dyestuffs. Copies of circulars describing these new products may be obtained on request.

National Erie Green GY—said to be the yellowest and brightest in the National line of direct greens. Its properties are similar to National Erie Fast Green CGB and National Erie Green MT, and is suitable for the dyeing of cotton, rayon, pure and tin-weighted silk. On half-wool and half-silk the animal fiber is dyed somewhat yellower and brighter than the vegetable fiber. This dyestuff is said to discharge readily with hydrosulfite and is recommended by the manufacturers as a ground color for white discharge effects on rayon, pure and tin-weighted silk.

National Wool Violet 5BN—an acid violet producing considerably bluer and brighter shades than National Wool Violet 4BN. It is very similar to the latter in all of its fastness properties but is said to leave celanese and rayon effects practically unstained. It is stated further that this dye possesses excellent fastness to perspiration, water and rubbing and very good fastness to washing and fulling. It is said to dye well from a neutral bath and is particularly well suited for the dyeing of tin-weighted silk. It is recommended by the manufacturers for the dyeing of wool, silk, glorias, etc., alone or in combination. Afterchroming renders the shade somewhat duller and redder but its fastness to fulling is said to be sufficient to make it of value as a shading product for mordant colors.

● M.I.T. SUMMER COURSES

Textile Microscopy, Textile Technical Analysis, and Textile Laboratory are the special summer courses being offered again this year by the Massachusetts Institute of Technology under the direction of Professor E. R. Schwarz. The work begins on July 24 and continues for six weeks ending on September 4.

Textile Microscopy consists of 30 lectures and 45 hours of laboratory. The lectures will be given at 10:15 each week day except Saturday and the laboratory will be offered from 1:00 to 3:30 on Monday, Wednesday, and Friday afternoons.

Textile Technical Analysis consists of 30 lectures given on each week day morning with the exception of Saturday from 9:15 to 10:15 and will cover the technique of the physical testing of textiles (exclusive of optical methods) and will also include discussion of methods of report writing, precision of measurements, graphical interpretation of data and the elements of fabric and yarn structure.

Textile Laboratory may be devoted to work in Textile Technical Analysis, to work in Textile Microscopy or both and is offered to fill a 15-hour per week schedule, arranged to suit the convenience of the student. Registration for the laboratory work is strictly limited and an early application is necessary to ensure membership in the group.

Excellent living facilities are available at very moderate cost in the new dormitory group. Reservations may be made at any time.

● CYANAMID SUMMER OPERATION

American Cyanamid Company and American Cyanamid & Chemical Corporation announced recently that, in line with the new general practice in the chemical industry, the New York offices at 30 Rockefeller Plaza, will be operated on Saturdays with a skeleton force only, for the handling of emergency orders. This plan will become operative on Saturday, June 1st, and extend to Saturday, September 28th, inclusive.

● GENERAL RELEASES

General Dyestuff Corp. announces release of the following new products. Copies of circulars describing fully these products may be obtained on request. Further releases are listed on page 174.

Anthralan Red G G—a new level dyeing acid red brought out by the I. G. and said to be of very good fastness to light. In other fastness requirements it is said to meet the general requirements for ladies' dress goods. Cotton, rayon or acetate effects are left clean. It is further said to be well suited for the printing of wool or silk and will discharge to a clean white with Rongalite C.

Chrysophenine Y A Extra Conc.—a well known direct yellow used for dyeing cotton, rayon and mixed fabrics. It is said to leave acetate white and to discharge easily.

OPEN FORUM

Rules under which this department of the REPORTER is conducted are as follows:

1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.

2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.

3. For each such reply published the Reporter will pay a minimum of $2.

4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.

5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.

6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.

Answers

20.—We have experienced partial color destroying action in basic color printing. The goods are folded face-to, and stored. The color destroying action is not uniform, showing bars, streaks, and blotches. When the material is baled this does not happen. Unfinished material does not show this result. No change in formulas over a period of years.—**G. O. Linberg.**

Answer—We have often seen instances of fading of dyes, in the manner described by querist, through presence in the same room as the affected goods of material which is slowly liberating sulfur dioxide fumes, such as white goods bleached with SO_2; or even the presence of hessian or woolen wrappers previously used by processors in covering up the white goods to protect them from falling smut, etc. Brown paper is sometimes stocked in quite large amounts in warehouses where dyed or printed piece goods are stored. One firm we know buys five tons of this paper at once. On entering the room, after it has been shut up over the week-end, one can smell a sharp odor quite appreciably. It has been proved time and again that SO_2 emanating from brown paper fades certain dyestuff.

Possibly the fading, etc., in querist's goods is due to reduction of the color as a consequence of omission to thoroughly wash out from the goods farinaceous thickeners, in cases where no preservative has been used to prevent bacterial action of this sort when farinaceous substances have been used during finishing. It is not stated what material the spoiled fabric is made of. This should have been done in order to obtain a helpful answer.—J. W.

22—I should be pleased to have some of the readers of the Dyestuff Reporter furnish a list of dyes satisfactory for use in transparent lacquers which are reasonably fast to light and as nearly permanent as possible.

I have understood that water glass is sometimes used for fixing dyestuffs upon wood surfaces.

If anyone has had experience along the lines mentioned above I should be pleased to hear whether such a process is satisfactory or not. Also, whether it gives a clear transparent coating of sufficient depth to correspond with a lacquer.—**K. J. L.**

Answer No. 2—For the cheapest work, basic dyestuffs are used for imparting a range of colors to lacquer. Some processors use the finely-ground color base; others prefer the ordinary commercial dyestuff. The colors are dissolved in warm industrial alcohol, then filtered. An endeavor to prepare too strong a solution will result in much of the supended dyestuff being left behind upon the filter. If a proportion of bleached or unbleached shellac is added to the strained solution of basic dye, a durable lacquer will result. To cheapen it, a proportion of common resin is used. A total weight of six ounces of shellac or resin per pint of color spirit produces a lacquer of medium body.

The writer prefers to use acid dyes for coloring lacquer and wood varnish of the spirit type. Radio Brown B and Radio Brown S, in combination, will yield a variety of useful brown shades on woodwork, which do not easily fade. For instance, the author has an oak cabinet which has been finished in medium brown color with the dyes in question, and no fading of the color is apparent after the lapse of five years. For three years the cabinet was kept near a large window through which the sun shone on bright days for several hours. The following acid dyes have been used by the writer for coloring spirit lacquer: Acid Violet 5BN, Fast Acid Violet A2R type, Radio Browns, Alizarine Cyanine Greens, Patent Blue A, Brilliant Milling Green B; Basic dyes: Malachite Green, Nigrosine (spirit soluble), Bismarck Brown, Auramine, Safranine, Rhodamine, Chrysoidine, Basic Black, Magenta, Methylene Blue, Methylene Green, Victoria Blue, Methyl Violet; Substantive dyes: Some of these will dissolve in spirit. The writer finds it best to dissolve them in water and brush the stain over the woodwork. When dry, apply several coats of clear lacquer.

For coloring oil and naphtha lacquers, oil base dyes are used. These are dissolved in the warm solvent.

then filtered and added to the solution of gum resin in oil or naphtha.

Some of the most permanent lacquer colors are prepared from finely-ground mineral or other pigments, such as Prussian blue, umber, burnt sienna, vandyke brown and lamp black or drop black. These, when ground in oil, are very suitable for coloring oil varnish. As regards the supplementary query about preparing a lacquer with water glass, this substance is of too caustic a nature to be safely used upon wood, in the author's opinion. Moreover, a great many dyestuffs would soon be decolorized in the presence of water glass, when this was being used at such a concentration as to produce an appreciable gloss upon the wood. Experiments we made with water glass disclosed that a fine white film eventually made its appearance on the surface of the woodwork and utterly ruined the finish and color. Furthermore, the water glass is apt to raise the grain of the timber when applied thus, rendering futile all the labor put forth in smoothing the furniture, etc.—J. W.

Unanswered Questions

17—We are in need of mathematical text books on problems pertaining directly to textile printing but so far have been unable to find anything on the subject. If you know of texts or problems in math. especially adapted to this field, I would more than appreciate suggestions.—**O. E. M.**

24—On numerous occasions, when a standing hydrogen peroxide bleach bath has not been used for four or five days, we have found that when adding peroxide to this bath or to fresh water in the same wooden tub, after running off the standing bath, immediately a violent hissing (the liberation of oxygen) takes place. Within an hour 25 pounds of 100 volume peroxide per 300 gallons of water has been used up.

The above happens in the presence or absence of silicate of soda or ammonia.

Once the above takes place it appears to be necessary to add sufficient peroxide to satisfy the "condition", after which the bath can be read, and made up to strength.

This abnormal condition is, of course, a waste of peroxide.

Have any readers any explanation as to the probable cause of the above taking place?—**T. F. A.**

25—Will you give what you consider the best method for bleaching worsted dress goods with Peroxide of Sodium and Peroxide of Hydrogen, showing formulae, with comparative costs, etc.—**D. G. H.**

26—I am interested in obtaining information concerning the composition of finishing compounds as applied to silk and rayon piece goods. Also methods for the laboratory analysis of such finishing compounds.—**S. A.**

27—Is there any satisfactory method for detecting the presence of Sulfur Black on a dark blue dyed fabric when a small amount of Sulfur Black has been added to the Sulfur Blue to deepen the shade?—**P. B. M.**

● SOUTHERN SECTION, RESEARCH INSTITUTE

The organization of a southern section of U. S. Institute for Textile Research, Inc., will be discussed at a luncheon meeting of the Institute's southern members, to be held at the Hotel Pionsett, Greenville, S. C., at 1. P.M., Thursday, April 11. Jno. W. Arrington, president of the Union Bleachery, Greenville, S. C., and a director of the Institute, has charge of the arrangements and will preside at the meeting.

Charles H. Clark, the Institute's secretary, will report on its activities with particular reference to the research on warp sizing that is now in progress at Massachusetts Institute of Technology with the financial aid of the Textile Foundation. All members of U. S. Institute who may be in Greenville for the Textile Exposition are invited to attend the luncheon meeting.

● SOUTHERN TEXTILE EXPOSITION

The Eleventh Southern Textile Exposition is being held during this week at Greenville, S. C. It is stated that in addition to cotton, considerable emphasis will be placed upon wool, silk and rayon. Exhibits cover all types of machinery and other products of general interest to the textile trade. Numerous organizations are planning to hold meetings during the week.

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

POSITION WANTED:— Graduate Chemist and Chemical Engineer, age 24, unmarried. Year and one-half experience as chemist in plant, dyeing and finishing rayons and silks. Salary secondary to placement with reliable concern. Write Box No. 853, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.